# EVALUATION OF MEMBRANE TREATMENT TECHNOLOGY TO OPTIMIZE AND REDUCE HYPERSALINITY CONTENT OF PRODUCED BRINE FOR REUSE IN UNCONVENTIONAL GAS WELLS

A Thesis

by

UCHE MARIAN EBOAGWU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2011

Major Subject: Petroleum Engineering

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Approved by:

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| Co-Chairs of Committee, | David Burnett |
| | Gene Beck |
| Committee Member, | Bryan Boulanger |
| Head of Committee, | Steven Holditch |

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# ABSTRACT

Evaluation of Membrane Treatment Technology to Optimize and Reduce Hypersalinity Content of Produced Brine for Reuse in Unconventional Gas Wells. (August 2011)

Uche Marian Eboagwu, B.S., University of Lagos, Nigeria

Co-Chairs of Committee: Mr. David Burnett
Dr. Gene Beck

Over 18 billion barrels of waste fluids are generated annually from oil and gas production in the United States. As a large amount of water is used for oilfield operations, treating and reusing produced water can cut the consumption of fresh water in well sites. This research has helped to develop a membrane process train for a mobile produced water treatment unit for treating oilfield produced brine for reuse.

To design the process train, over 30 sets of combination tests at pilot laboratory scale were performed using pretreatment, microfiltration and nanofiltration processes. Membrane performance was selected based on high flux separation efficiency, high tolerance for solids and fluid treatments. Over 95 % solids rejection and greater than 80 % oil removal efficiency were obtained in all these tests.

Process train (pre-treatment and membrane) performance was monitored by chemical analysis of permeate models fitting experimental data for the process. From the results, hydrocarbon rejection was analyzed; total organic carbon rejection was 47.9 %, total carbon content averaged 37.3 % rejection and total inorganic carbon rejection was at 3.66 %. BTEX removal efficiency ranged from 0.98 % to 52.7 % with the progressive

pretreatment methods of using cartridge filters. The nanofiltration membrane showed significant reduction in total dissolved solids and in both anionic and cationic species. The process train is seen to follow a sequence of treatment from cartridge and oil removal filter treatment to microfiltration treatment to ultrafiltration, followed by nanofiltration for the purpose of this research. Further research still needs to be done on to determine the kind of analytical test which will give real time feedback on effectiveness of filters.

In summary, the process train developed by TAMU-GPRI possesses distinct advantages in treating oilfield produced brine using membrane technology. These advantages include high quality of permeate, reduced sludge and the possibility of total recycle water systems. The small space requirement, moderate capital costs and ease of operation associated with the use of the mobile unit membrane technology also makes it a very competitive alternative to conventional technologies.

# DEDICATION

This thesis is dedicated to the Almighty God, for the love, grace, wisdom, and protection upon me until this very moment in my life.

It is also dedicated to my loving, caring, and supportive family, for all their prayers and support in my course of completing this work. You all mean so much to me.

Finally, I dedicate this work to all my friends with whom we shared successes and failures, laughs and sorrow, it has not been easy, but I am glad we made it thus far, for sure the sky is the limit for us all.

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to my advisor, Mr. David Burnett for his invaluable guidance and support through my studies at Texas A&M University. His advice, dedication and motivation have influenced my life while working under his tutelage.

I would also like to thank Dr. Gene Beck and Dr. Bryan Boulanger for serving as co-chair and member of my graduate advisory committee respectively.

Thank you to Carl Vavra of Separation Sciences Department for successful completion of this thesis and for sharing and always bringing new ideas and insights to problems, and also to Frank Platt, Keith McLeroy, and Barbi Wood I say a very big thank you. My appreciation also goes to MiSwaco team for funding this project and for providing technical advice.

And finally, thank you once again to Mr. David Burnett for funding my graduate studies at Texas A&M University through his research.

# NOMENCLATURE

| | |
|---|---|
| API | American Petroleum Institute |
| BTEX | Benzene Toluene Ethylbenzene |
| CA | Cellulose Acetate |
| CF | Concentration Factor |
| CF | Crossflow |
| Cu | Copper |
| DOE | Department of Energy |
| ED | Electrodialysis |
| EIA | Energy Information Administration |
| EPA | Environmental Protection Agency |
| FERC | Federal Energy Regulatory Commission |
| fΔp | Function of Pressure Change |
| gpm | Gallon Per Minute |
| GPRI | Global Petroleum Research Institute |
| H | Hour |
| HARC | Houston Advanced Research Center |
| $H_2S$ | Hydrogen Sulphide |
| Hp | Horse Power |
| J | Flux |
| LANL | Los Alamos National Laboratory |
| LMH | Liters Per Meter Squared Per Hour |

| | |
|---|---|
| $m^2$ | Meter Squared |
| MF | Microfiltration |
| Mg/L | Milligram Per Liter |
| MWCO | Molecular Weight Cut-Off |
| ND | Not Detectable Within Reporting Limit |
| NF | Nanofiltration |
| NTU | Nephelometric Turbidity Unit |
| $^{O}$ C | Degree Celsius |
| $^{O}$ F | Degree Fahrenheit |
| PGC | Potential Gas Committee |
| Ppm | Parts Per Million |
| R | Rejection Rate |
| Re | Reynold's Number |
| RO | Reverse Osmosis |
| SMZ | Surfactant Modified Zeolite |
| SPE | Society of Petroleum Engineers |
| TAMU | Texas A&M University |
| Tcf | Trillion Cubic Foot |
| TDS | Total Dissolved Solids |
| TIC | Total Inorganic Carbon |
| TMP | Transmembrane Pressure |
| TOC | Total Organic Carbon |

| | |
|---|---|
| TOGA | Total Oil and Grease |
| TPH | Total Petroleum Hydrocarbon |
| UF | Ultrafiltration |
| UIC | Underground Injection Control |
| USGS | United States Geological Survey |
| UV | Ultraviolet |
| VOC | Volatile Organic Compound |
| Zn | Zinc |

# TABLE OF CONTENTS

Page

CHAPTER Page

# LIST OF FIGURES

FIGURE Page

# LIST OF TABLES

# CHAPTER I

# INTRODUCTION

## 1.1 Unconventional Resources – Background State of the Industry

Unconventional natural gas resources constitute a large proportion of the natural gas that is left to be extracted in North America, and is playing an ever increasing role in supplementing the nation's natural gas supply. In the past, unconventional gas resources were more difficult, and less economically practical, to extract, usually because the technology to reach it had not been developed fully, or was too expensive. As technology has advanced and new methods of extracting and using this natural gas have been developed, the resource potential of unconventional natural gas has grown enormously. A large favorable resource base, advances in knowledge, and steady progress in extraction technology has enabled significant portions of this resource to be converted to producible reserves at economic flow rates or economic volumes.

Unconventional oil and gas resources can be characterized by either intractable rock with very low permeability or intractable fluids (or in the case of gas hydrates, solids) where some form of stimulation is typically required for commercial production. These resources overturn many of the exploration and production patterns applied to conventional hydrocarbons.

_____

This thesis follows the style of *SPE Production & Operations*.

Economically speaking, unconventional hydrocarbons are usually (but not always) characterized by high break-even product prices and as such become the focus of attention as conventional resource supplies diminish or become unavailable to the multinational companies. Exploration, drilling and production of shale gas plays such as the Barnett, Marcellus, Fayetteville, Haynesville and recently the Eagle Ford have transformed the unconventional gas industry by creating jobs opportunities and royalty income.

Shale is a very fine-grained sedimentary rock, which is easily breakable into thin, parallel layers. It is a very soft rock, but does not disintegrate when it becomes wet. Shale can contain natural gas, usually when two thick, black shale deposits 'sandwich' a thinner area of shale. Because of some of the properties of shale, the extraction of natural gas from shale formations is more difficult and thus expensive than extraction of conventional natural gas. Most of the natural gas containing Devonian shale in the U.S. is located around the Appalachian Basin (Wikipedia). Figure 1.1 shows the major shale gas basins in United States.

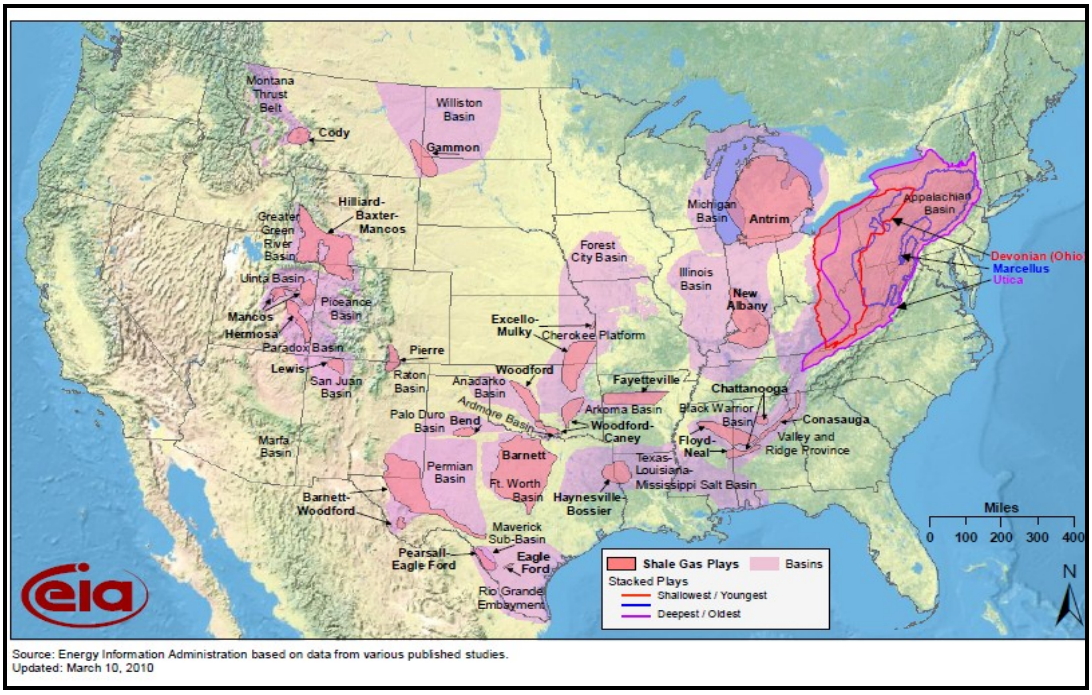


**Fig. 1.1—Major Shale Gas Basins in United States**

Estimates of the amount of natural gas contained in shales are large and their potential as a natural gas supply is increasing, given an adequate technological, economical, and environmental conditions. Figure 1.2 below shows a logarithmic increase in resources and corresponding reserves as technology has developed and the investment opportunity realized.

At the core of shale gas development are two key primary enabling technologies currently in use: horizontal drilling and multi-stage hydraulic fracturing. To produce gas at an economic flow rate and produce commercial volumes of natural gas, wells in unconventional reservoirs must be designed in such a way as to contact a large surface area of rock. Long horizontal laterals and multi-stage fracs accomplish this economically.

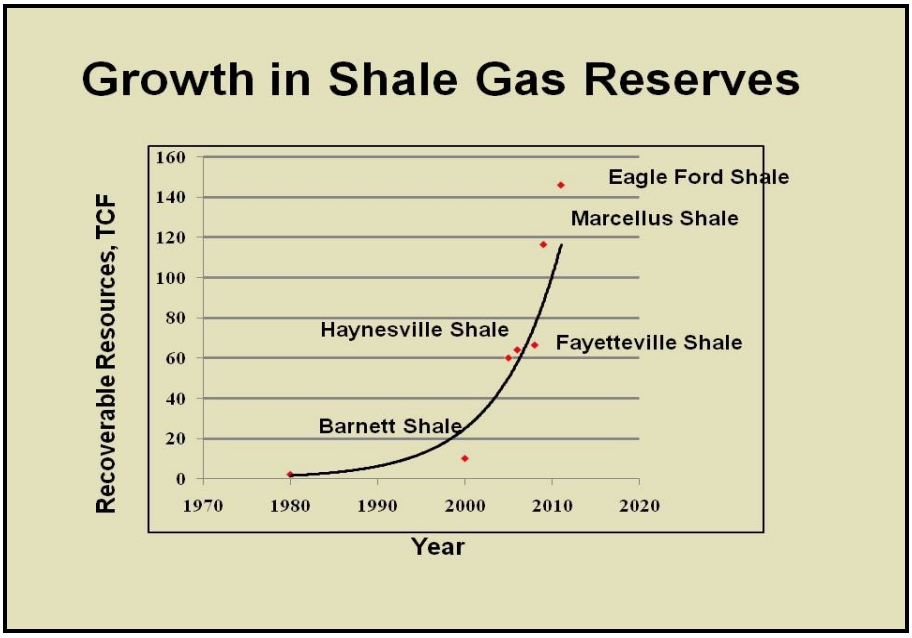


**Fig. 1.2—Growth in Shale Gas Reserves**

There are six main categories of unconventional natural gas. These are deep gas, tight gas, shale gas, coalbed methane, geopressurized zones, and Arctic and sub-sea hydrates.

### 1.1.1 Deep Natural Gas

Deep natural gas is natural gas that exists in deposits very far underground, beyond 'conventional' drilling depths. This gas is typically 15,000 feet or deeper underground, quite a bit deeper than conventional gas deposits, which are traditionally only a few thousand feet deep, at most. Deep gas has, in recent years, has become more conventional. Deep drilling, exploration, and extraction techniques have substantially improved, making drilling for deep gas economical. However, deep gas is still more

expensive to produce than conventional natural gas, and as such, economic conditions have to be such that it is profitable for the industry to extract from these sources.

### 1.1.2 Tight Natural Gas

This is gas that is found in a very tight formation underground, trapped in unusually impermeable, hard rock, or in a sandstone or limestone formation that is unusually impermeable and non-porous (tight sand). In a conventional natural gas deposit, once drilled, the gas can usually be extracted quite readily and easily. Several techniques exist that allow natural gas to be extracted, including fracturing and acidizing. However, these techniques are also very costly. Like all unconventional natural gas, the economic incentive must be there to encourage companies to extract this costly gas instead of more easily obtainable, conventional natural gas.

Tight gas makes up a significant portion of the nation's natural gas resource base, with the Energy Information Administration (EIA) estimating that, as of January 2009, 310 tcf (trillion cubic foot) of technically recoverable tight natural gas exists in the U.S. This represents over 17% of the total recoverable natural gas in the United States, and is an extremely important portion of natural gas resources.

### 1.1.3 Shale Gas

Natural gas can also exist in shale deposits. Shale is a very fine-grained sedimentary rock, which is easily breakable into thin, parallel layers. It is a very soft rock, but does not disintegrate when it becomes wet. These shales can contain natural gas, usually when two thick, black shale deposits 'sandwich' a thinner area of shale.

Although estimates of the amount of natural gas contained in these shales are high, it is expected that only about 10 percent of the gas is recoverable. However, their potential as a natural gas supply is still very promising, given an adequate technological and economic environment. As of November 2008, Federal Energy Regulatory Commission (FERC) estimated that there are 742 tcf of technically recoverable shale gas in the United States, representing a large and growing share of total recoverable resources.

### 1.1.4 Coal Bed Methane

Coal is a fossil fuel formed underground under similar geologic conditions as natural gas and oil. These coal deposits are commonly found as seams that run underground, and are mined by digging into the seam and removing the coal. Many coal seams also contain natural gas, either within the seam itself or the surrounding rock. This coalbed methane is trapped underground, and is generally not released into the atmosphere until coal mining activities unleash it.

This methane can be extracted and injected into natural gas pipelines for resale, used as an industrial feedstock, or used for heating and electricity generation. The Potential Gas Committee (PGC) estimates that 163.0 tcf of technically recoverable coalbed methane exists in the United States, making up 7.8% of the total natural gas resource base. Figure 1.3 shows the resource triangle for oil and gas reservoirs.

### 1.1.5 Gas Hydrates

Gas hydrates are the most recent form of unconventional natural gas to be discovered and researched. These formations are made up of a lattice of frozen water,

which forms a sort of cage around molecules of methane. These hydrates look like melting snow and were first discovered in permafrost regions of the Arctic. Methane hydrates is estimated to range from 7,000 tcf to over 73,000 tcf. The United States Geological survey (USGS) estimates that methane hydrates may contain more organic carbon than the world's coal, oil, and conventional natural gas combined.

### 1.1.6 Geopressurized Zones

Geopressurized zones are natural underground formations that are under unusually high pressure for their depth. These areas are formed by layers of clay that are deposited and compacted very quickly on top of more porous, absorbent material such as sand or silt. Water and natural gas that is present in this clay is squeezed out by the rapid compression of the clay, and enters the more porous sand or silt deposits. This natural gas, due to the compression of the clay, is deposited in this sand or silts under very high pressure, hence the term 'geopressure'. In addition to having these properties, geopressurized zones are typically located at great depths, usually 10,000-25,000 feet below the surface of the earth. The combination of all of these factors makes the extraction of natural gas in geopressurized zones quite complicated.

However, of all of the unconventional sources of natural gas, geopressurized zones are estimated to hold the greatest amount of gas. Most of the geopressurized natural gas in the U.S. is located in the Gulf Coast region. The amount of natural gas in these geopressurized zones is uncertain. However, experts estimate that anywhere from 5,000 to 49,000 Tcf of natural gas may exist in these areas! Given the current technically

recoverable resources are around 1,100 Tcf, geopressurized zones offer an incredible opportunity for increasing the nation's natural gas supply.

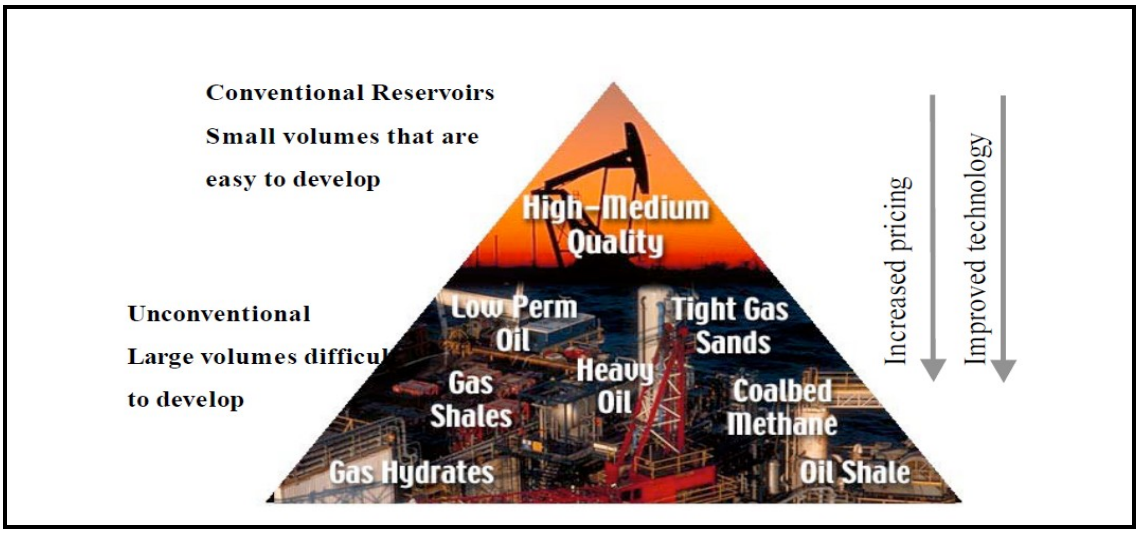


**Fig. 1.3—The Resource Triangle for Oil and Gas Reservoirs (Source: Working Document of the National Petroleum Council (NPC) Global Oil and Gas Study)**

## 1.2 Hydraulic Fracturing of Unconventional Resources

Hydraulic fracturing often known as “fracing” is a stimulation process used in completing wells in shale reservoirs. It involves pumping a fluid into a well at very high pressure to create cracks/fractures in the reservoir rocks, thereby creating additional permeability in a producing formation. In coming decades, the use of this technology will allow production of natural gas from low permeability reservoirs, coal bed methane reservoirs, and shale gas reservoirs from virtually every major oil and gas basin in the world.

The purpose of a fracture is to alter the flow pattern in the reservoir to increase

the oil and gas flow rates. The process of hydraulic fracturing as typically used for shale gas development involves the pumping of tens of thousands of barrels of fracturing fluid under high pressure into the target shale zone to generate fractures or cracks. Once the pumping of fluids has stopped, the sand remains in place allowing fluids both gas and water to flow back to the wellbore. For shale gas development, fracture fluids are primarily water based fluids mixed with additives that help the water to carry sand proppant into the fractures. Water and sand make up over 98% of the fracture fluid composition, with the rest consisting of various chemical additives that improve the effectiveness of the fracture job. Figure 1.4 shows a typical composition of fracture fluid for shale gas development.

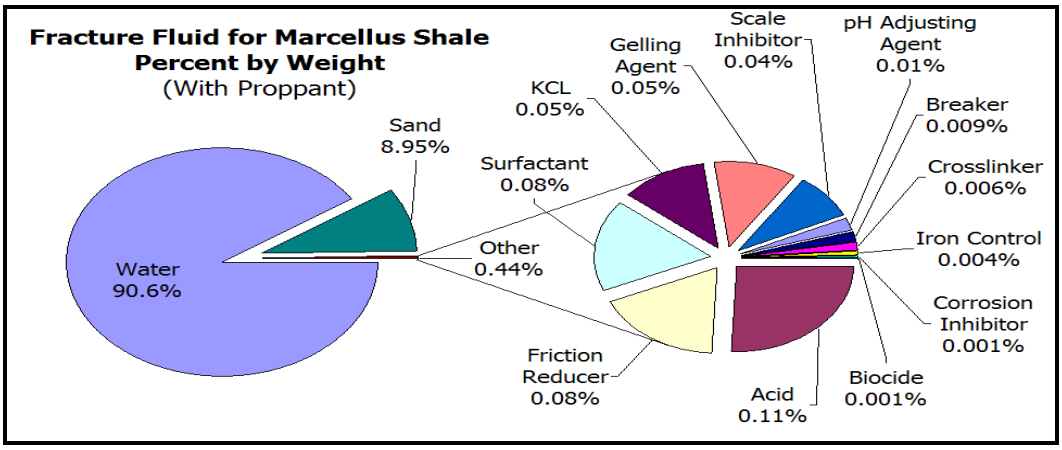


**Fig. 1.4—Fracture Fluid Composition (Source : (Arthur et al., 2009) )**

Fig.1.4 shows that water is the primary component for fracturing treatments used in shale gas plays. Availability of water and water management is a distinguishing factor between various shale gas plays across the country. With fracture treatments requiring

tens of thousands of barrels of water per stage to stimulate fractures, operators within shale gas plays are pressed to identify a number of unique ways of acquiring fresh water. Finding enough water for hydraulic fracturing is an issue and operators are forced to recycle. These volumes of fluid require economical and environmentally friendly methods of treatment so it can be re-used or disposed safely. Fracturing operations consume millions of gallons of fresh water and generate millions of gallons of fracture fluid backflow in wastes.

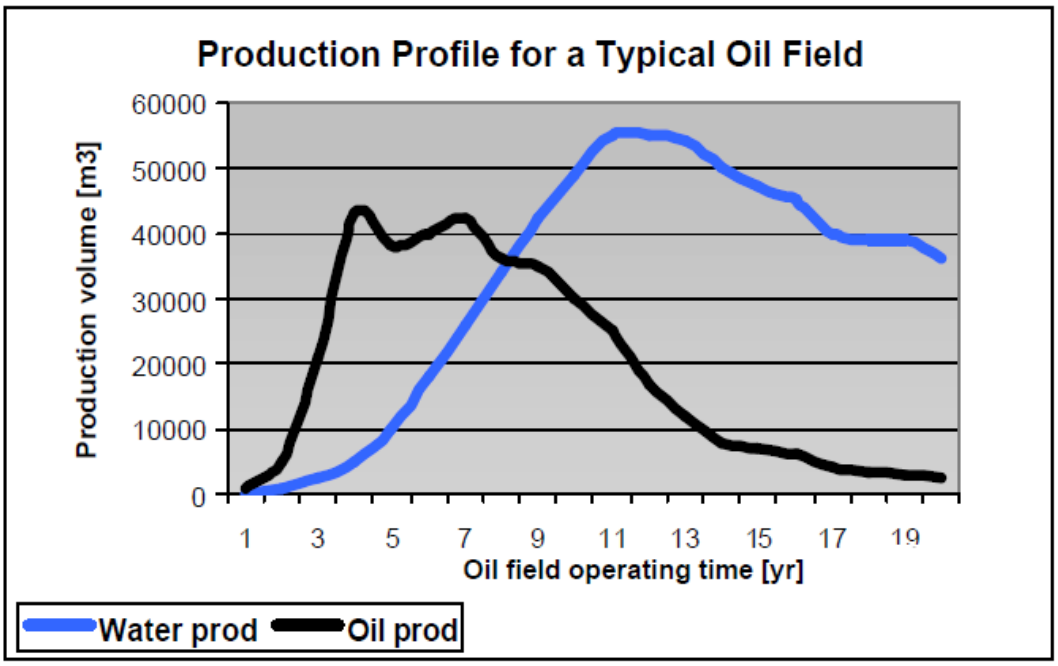


**Fig. 1.5—Water Generation in a Typical Oil Field**

Figure 1.5 shows the production profile of a typical oil field over a period of years. To mitigate the problem of this large volume of produced water and frac flow back water, approaches that can be used include:

- Inject the water back into disposal wells after de-oxygenation of the produced water (class II injection wells regulated by the Environmental Protection Agency (EPA) through the Underground Injection Control (UIC) regulations. This water can then be used for enhanced recovery operations by injecting them into producing formations through the water-flooding stimulation process to help move crude oil to wells for collection.
- Inject the water into separate salt water disposal wells.
- A good alternative for disposal of produced water would be to send it back into the reservoir where it came from as part of the pressure support, or to another suitable formation. Unfortunately this requires extensive treatment prior to re-injection and due to high costs it is an economically viable alternative mainly for fields with large water production. Reinjection could also cause degradation of the reservoir production quality and productivity.
- Treat the water for disposal and/or reuse.

Discharging produced water can pollute surface and underground water and soil. In order to meet environmental regulations, the industry is turning to recycling and reuse of frac flowback water. However, reuse without treatment may cause formation damage to the well. Thus the combined focus of A&M Petroleum Engineering Department's program treatment is to improve effluent characteristics using methods which will meet industry's discharge limit, reuse and recycle standards, and have small footprint.

Because produced water characteristics vary from gas fields to oil fields and from one well to another and depending on the age of the well, a unique universal

technique cannot be recommended for achieving all environmental standards, recycling and reuse requirements. Cost-effective management of produced water improves the profitability of natural gas and oil producers by reducing the costs associated with the disposal of produced water.

## 1.3 Research Objectives

This research highlights the use of membrane technology in treating oilfield produced brine in a responsible environmentally friendly and safe manner. It aims to water-disposal volumes through the re-use of treated produced water for other rig operations, reduced disposal requirements, and reduced environmental footprint in well sites. This proposed water treatment and management alternative is developed as a need to meet water requirement and supply at well sites as gas is being produced from new unconventional reserves in which large volumes of water resources are being used, and where obtaining this large water volume and managing them is posing a problem to producers.

## 1.4 Need for Small Footprint Systems

The need for small footprint systems in well sites is being investigated by The Environmentally Friendly Drilling (EFD) Systems Program which is operated by the Houston Advanced Research Center (HARC) and Texas A&M University, along with industry sponsors, the public and various environmental organizations. The EFD Technology Integration Program (TIP) addresses issues on the development of unconventional gas resource in an environmentally safe manner through the use

advanced technologies such as low-impact technologies that reduce the footprint of drilling activities, use of light weight drilling rigs with reduced emission engine packages, on-site waste management, drilling system optimization to fit the needs of a specific development sites. The aim of the EFD program is to significantly reduce the impact of petroleum drilling and production operations in well sites while at the same time making the system cost effective. The EFD TIP approach is currently in use in actual gas shale development such as the Eagle Ford Shale.

One of the largest projects within the EFD program is the effort to reduce environmental problems associated with large volume of water used in well construction. Due to the size of operations involved in producing unconventional reserves, major issues associated with these are land use and protection of water resources and emissions which might affect air quality as in the Eagle Ford shale play. TAMU-GPRI is projecting the use of a series of continuous membrane filtration processes to pretreat and desalinate water prior to disposal.

## 1.5 Goals of the Process Train

Texas A&M is attempting to use membrane filtration as an alternative to other conventional methods of produced water treatment such as flocculation, precipitation, and filtration. The benefit of this work includes the small footprint size of membrane technology, low weight and low energy requirements of the process, high throughput rates associated with using the technology, and no treatment chemical addition required. The selection of this technology is based on economics, versatility, small size,

compactness, and ease of usage. Membrane processes also offer other advantages over conventional treatments. They reduce the number of unit processes in treatment systems for clarification and disinfection and increase the potential automation and plant compactness. They produce less sludge than conventional processes like flocculation and chemical treatment methods because they limit the use of chemicals such as coagulants or polymers.

Best practices dictates produced water is cleaned to an extent, the level of cleaning dependent on the intended use and current discharge regulations. Without using additional expensive chemicals for coagulation or settling, current technologies used to treat produced water are not capable of achieving recently required standards of purity (Ashaghi et al., 2007). Operators have turned to membrane filtration schemes due to their potential to minimize additional costs and disposal issues associated with current technologies.

The goal of the process train used in this research work is to remove the constituents of produced water to an appreciable and significant extent for reuse. This will be achieved through a continuous treatment process using membranes.

Membrane-based separation is a pressure-driven process that relies on the pore size of the membrane to separate the feed-stream component (Sonune and Ghate, 2004). Membranes are thin films of synthetic organic or inorganic materials which selectively separate a fluid from its components based on the physical size of pores and contaminants. Each membrane process is optimized by pore size for a particular water treatment function. Microfiltration (MF) is separation of suspended particles,

ultrafiltration (UF) is the separation of macromolecules, and reverse osmosis (RO) is the separation of dissolved and ionic components (Madaeni, 1999). Media filters removed oil, MF and UF mostly effectively removed suspended particles with NF softening the water by removing calcium and magnesium ions.

The use of membrane systems to treat waste streams avoids some of the problems in waste brine processing for the operator. Conventional treatment of produced water includes gravity separation and skimming, dissolved air floatation, de-emulsification, coagulation and flocculation (Cheryan and Rajagopalan, 1998). However, disadvantages associated with these unit operations include:

- gravity separation: may not produce effluents that meet discharge limits
- use of chemical emulsion breakers require customization for each site to determine the types and quantities of chemical needed
- large volumes of sludge are often produced
- operational costs can be high

Olatubi et al.(2008) used membrane filtration to achieve a 60 % reduction in waste volume when treating drilling wastes and oilfield produced water. Burnett (2004) showed that combined pretreatment and RO technology are cost-effective methods for desalinating produced water to a total dissolved solids (TDS) of less than 10,000 ppm. Bilstad and Espedal (1996) compared MF and UF membranes in studies to treat North Sea oilfield-produced water and their results showed that UF, but not MF, could meet effluent standards for total hydrocarbons, suspended solids, and dissolved constituents. In UF membranes, treatment with molecular weight cut-off (MWCO) between 100,000

and 200,000 Daltons was deplored, where total hydrocarbon concentrations could be reduced to 2 mg/L from 50 mg/L (96% removal). Benzene, toluene, and xylene (BTX) were reduced by 54%, and some heavy metals like Cu, and Zn were removed up to 95%. This enhanced recovery was achieved because of the tighter membrane used and as a result of the pore size of the membrane.

## 1.6 Technologies Available for Produced Water Treatment

There are a number of methods used for produced water treatment, each having its respective advantages and disadvantages. No single technique currently used is suitable for all needs. In 1995, the American Petroleum Institute (API) made its recommendation for the best available technology for produced water management on offshore gas and oil installations as follows:

- **Gravity Based Separation (Flotation)**

  In this process, produced water treatment takes place in gravity based equipment, mostly huge horizontal tanks at different pressure, with differences in density of the two liquids being the main driver for separation. Flotation of lighter components (oil) is enhanced by means of finely distributed gas bubbles going out of solution (pressure reduction) and parallel plate packages installed diagonally in the separation vessel. Gravity separation has the disadvantage of not producing effluents that meet discharge limits and treated water that meet reuse quality, thus requiring additional downstream ancillaries.

- **Coalescence (Enhanced Oil Separation)**

  This method is based on the coalescing of dispersed oil droplets, often prior to cyclonic separation. The devices are installed upstream of the cyclonic vessels to increase oil droplet diameters which will result in better separation degree in hydro cyclones. The process of coalescence can be accelerated by different means. One method is to install special fibrous media in the piping or in the hydro cyclone vessels that attracts oil droplets and promotes coalescence into larger aggregates. A major disadvantage of this type of treatment is that it has no effect on removing dissolved hydrocarbons and the fiber media is sensitive to fouling and any abrasive elements such as sand in the water.

- **Carbon Adsorption (Modular Granular Activated Carbon Systems)**

  Carbon adsorption removes hydrocarbons and acid, base and neutral compounds. It has low energy requirements, higher throughput than other similar treatments, (except biological) and treats a broad range of contaminants; moreover it is very efficient at removing high molecular weight organics.

  Among potential disadvantages are fouling of carbon granules is problematic, waste stream of carbon and backwash, and the requirement of some pre-treatment of produced water stream.

- **Air Stripping (Packed Tower with Air Bubbling Through the Produced Water Stream)**

  Potential to remove 95% of volatile organic compounds (VOCs) as well as benzene, toluene, naphthalene, and phenols; $H_2S$ and ammonia can be stripped

with pH adjusting. Higher temperature improves removal of semi-volatiles. The equipment is generally small size, low weight with low energy requirements. Disadvantages: Can be fouled by oil; risk of iron and calcium scale formation; generates an off-gas waste stream that may require treatment; requires some pre-treatment of produced water stream.

- **Ultra-Violet Light (Irradiation by UV Lamps)**

  Ultra-violet light destroys dissolved organics and both volatile and non-volatile organic compounds, including organic biocides; does not generate additional waste stream; handles upset or high loading conditions.

  The disadvantages of this method includes not treating ammonia, dispersed oil, heavy metals, or salinity, it has relatively high energy requirements, UV lamps may become fouled, residues may be toxic if peroxide is used, and it requires some pre-treatment of produced water stream.

- **Chemical Oxidation (Ozone and/or Hydrogen Peroxide Oxidation)**

  Chemical oxidation removes hydrogen sulfide ($H_2S$) and particulates, treats hydrocarbons, acid, base and neutral organics, volatiles and non-volatiles, has low energy requirements if peroxide system is used and the operation is straightforward.

  High energy inputs for ozone system, oil may foul catalyst, may produce sludge and toxic residues, the requirement of some pre-treatment of produced water stream are some of the disadvantages of this treatment method.

- **Biological Treatment (Aerobic System with Fixed Film Biotower or Suspended Growth)**

  Biological treatment treats biodegradable hydrocarbons and organic compounds, $H_2S$, some metals and, in some conditions, ammonia; "fairly low" energy requirements; handles variable loadings, if acclimated.

  The major disadvantages of this treatment method include that it is capital intensive and the build-up of oil and iron hinders biological activity, aeration causes calcium scale formation, produces gas and sludge requiring treatment, requires some pre-treatment of feed.

- **Chemical Injection (Coagulation/Flocculation)**

  Coagulation and flocculation are often used as synonyms. They refer to the whole process of particle agglomeration. Specifically, coagulation is a chemical process used to destabilize colloidal particles by the addition of a chemical agent which generates positively charged ions in water, which contains negatively charged colloids reducing their charge densities. This creates a reduction in the repulsion between the particles. Flocculation is the aggregation of particles in suspension. This agglomeration is a function of the Van der Waals forces. Formation of flakes can occur spontaneously only through the successive collisions between particles, if the system has energy available to do so, as through agitation. However, very intense stirring can disaggregate the flakes that are spontaneously formed, in which case there would be no need of such strong agitation as that used in the mixing operation. Many coagulating agents are used

in processes for treating water, such as inorganic coagulants, e.g. salts of aluminum and iron, and synthetic and natural organic polymers.

Addition of chemical is an additional cost to treatment cost and the volume of sludge generated is a major issue and requires treatment of the generated sludge. Aluminum is not biodegradable and can cause disposal problems.

- **Membrane Filtration (NanofIltration and Reverse Osmosis Polymeric Membranes)**

  Effective removal of particles, dispersed and emulsified oil, small footprint size, low weight and low energy requirements, and high throughput rates are some advantages of this treatment method.

  The disadvantages of the method are that it doesn't remove volatiles or low molecular weight compounds, oil, sulfides or bacteria may foul membrane, which requires daily cleaning, effluent by-product may contain radioactive material, requires some pre-treatment of feed stream.

  This recommendation makes clear that required pretreatment of produced water stream (feed) is a major disadvantage of all treatment technologies. However, the combining of different technologies affords the possibility to reduce the pollutants in produced water to almost undetectable levels.

- **Electrodialysis (ED)**

  Most salts dissolved in water are ionic. These ions are attracted to electrodes with an opposite electric charge. In ED, membranes that allow either cations or anions, but not both, to pass are placed between a pair of electrodes. These

membranes are arranged alternately. A spacer sheet that permits feed water to flow along the face of the membrane is placed between each pair of membranes.

- **Evaporation**

  This is a technique in which latent heat is provide to the feed water to generate vapor which is then condensed into pure water. The residual stream contains high concentration of salts/solids from the produced water. This method eliminates the majority of chemical or physical pretreatment.

- **Freeze Thaw Evaporation**

  Produced water is first stored in a holding pond until air temperatures drop below 0° C (32° F). The water is then removed from the pond using pumps and sprayed onto a separate freezing pad which consists of an elevated pipe grid with strategically placed sprinklers. These sprinklers can be raised as the ice builds up on the pipe grid. The unfrozen brine water drains from the ice grid and is separated using conductivity-controlled valves. The concentrated brine water is then transported to separate storage ponds for either secondary treatment or for disposal. Crystal Solutions, LLC, a joint venture of Gas Technology and BC Technologies, utilized this method for produced water treatment at its first major commercial treatment facility near Wamsutter, Wyoming.

- **Ion Exchange**

  This process effectively removes arsenic, heavy metals, nitrates, radium, salts, uranium, and other elements from produced water. It is a reversible chemical reaction where positively or negatively charged ions present in the water are

replaced by similarly charged ions present within the resin. The resins immersed in the water are either naturally occurring inorganic zeolites or synthetically produced organic resins. When the replacement ions on the resin are exhausted, the resin is recharged with more replacement ions.

## 1.7 Characteristics of Produced Water

Produced water is a mixture of organic and inorganic materials (Veil and Clark, 2010) . Oilfield produced water is used in the oil industry to describe the water that is produced along with the oil and/or gas, and it may contain formation water, flow back fluids, surface water, and water from any other sources. Factors such as geological location and formation of the field, lifetime of the field reservoirs, and type of hydrocarbon produced from the reservoir affect the physical and chemical properties of produce water which may vary considerably. The characteristics of produced water depends on the nature of the producing storage formation from which they are withdrawn, the operational conditions, and chemicals used in process facilities. The major constituents of produced water are:

- Dissolved and dispersed oil compound: Oil is a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols. Water cannot dissolve all hydrocarbons, so most of the oil is dispersed in water (Ekins et al., 2007). The amounts of dissolved and suspended oil present in produced water (prior to treatment) are related to factors such as oil

constituents, pH, salinity, TDS (total dissolved solids), temperature, oil/water ratio, type and quantity of oilfield chemicals, and type and quantity of various stability compounds, e.g. waxes, asphaltenes, fine solids.

- Dissolved formation minerals: Inorganic dissolved compounds in produced water include anions and cations, heavy metals, and radioactive materials. Produced water contains a wide range of both cations and anions. Cations and anions affect produced water chemistry in terms of buffering capacity, salinity, and scale potential. Salinity is due to dissolved sodium and chloride and is less contributed by calcium, magnesium, and potassium. Salt concentration in produced water may vary from 1,000 mg/L to 250,000 mg/L.
- Various natural inorganic and organic compounds or chemical additives used in drilling and operating the well. The concentration of production chemicals in produced water may be as low as 0.1 ppm (Veil and Clark, 2010).
- Production solids may include formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes.
- Naturally occurring radioactive material (NORM): the source of radioactivity in scale is from radioactive ions, primarily radium that is co-precipitated from produced water along with other types of scale forming ions. Barium sulfate is the most common scale co-precipitate. Radium-226 and Radium-228 are the most abundant NORM in produced water. There is a strong correlation between concentrations of barium and radium isotopes.
- Oil and grease is a measure of the organic chemical compounds.

- Dissolved gases include $CO_2$, $O_2$, and $H_2S$. These are common gases present in produced water.

**Table 1.1—Summary of Oilfield Produced Water Parameters in the World (Source: Tibbetts P.J.C et al 1992).**

| Parameter | Values | Heavy metal | Values (mg/L) |
|---|---|---|---|
| Density (kg/m$^3$) | 1014–1140 | Calcium | 13–25800 |
| Surface Tension (dynes/cm) | 43–78 | Sodium | 132–97000 |
| TOC (mg/L) | 0–1500 | Potassium | 24–4300 |
| COD (mg/L) | 1220 | Magnesium | 8–6000 |
| TSS (mg/L) | 1.2–1000 | Iron | <0.1–100 |
| pH | 4.3–10 | Aluminum | 310–410 |
| Total oil (IR; mg/L) | 2–565 | Boron | 5–95 |
| Volatile (BTX; mg/L) | 0.39–35 | Barium | 1.3–650 |
| Base/neutrals (mg/L) | <140 | Cadmium[a] | <0.005–0.2 |
| (Total non-volatile oil and grease by GLC/MS) base (µg/L) | 275 | Chromium | 0.02–1.1 |
| Chloride (mg/L) | 80–200,000 | Copper | <0.002–1.5 |
| Bicarbonate (mg/L) | 77–3990 | Lithium | 3–50 |
| Sulfate (mg/L) | <2–1650 | Manganese | <0.004–175 |
| Ammoniacal nitrogen (mg/L) | 10–300 | Lead[a] | 0.002–8.8 |
| Sulfite (mg/L) | 10 | Strontium | 0.02–1000 |
| Total polar (mg/L) | 9.7–600 | Titanium | <0.01–0.7 |
| Higher acids (mg/L) | <1–63 | Zinc[a] | 0.01–35 |
| Phenols (mg/L) | 0.009–23 | Arsenic[a] | <0.005–0.3 |
| VFA's (volatile fatty acids) (mg/L) | 2–4900 | Mercury | <0.001–0.002 |
| | | Silver[a,b] | <0.001–0.15 |
| | | Beryllium | <0.001–0.004 |

[a] (Analyzed by atomic absorption) [b] (Value should be regarded as minimum due to poor solubility)

Table 1.1 above is a summary of oilfield produced water parameters in the world as compiled by Tibbetts et al. The constituents of natural gas produced water are shown in Table 1.2.

**Table 1.2—Constituents of Natural Gas Produced Water (Source: Fakhru'l-Razi et al. 2009). Data in mg/L; pH is Presented in Standard Unit.**

| Parameter | Minimum value | Maximum value | Parameter | Minimum value | Maximum value |
|---|---|---|---|---|---|
| pH[a] | 4.4 | 7.0 | Iron[a] | ND | 1100 |
| pH[b] | 3.1 | 6.47 | Iron[b] | 39 | 680 |
| Conductivity[a] (umhos/cm) | 4200 | 180,000 | Lead[b] | <0.2 | 10.2 |
| Conductivity[b] (umhos/cm) | 136,000 | 586,000 | Lithium[b] | 18.6 | 235 |
| Alkalinity[b] | 0 | 285 | Magnesium[a] | 0.9 | 4300 |
| TDS[a] | 2600 | 310,000 | Magnesium[b] | 1300 | 3900 |
| TDS[b] | 139,000 | 360,000 | Manganese[a] | 0.045 | 6.5 |
| TSS[a] | 14 | 800 | Manganese[b] | 3.59 | 63 |
| TSS[b] | 8 | 5484 | Nickel[a] | ND | 0.02 |
| $BOD_5$[a] | 75 | 2870 | Nickel[b] | <0.08 | 9.2 |
| COD[a] | 2600 | 120,000 | Potassium[b] | 149 | 3870 |
| Aluminum[a] | ND | 0.4 | Silver[b] | 0.047 | 7 |
| Aluminum[b] | <0.50 | 83 | Sodium[a] | 520 | 45,000 |
| Arsenic[a] | 0.004 | 1 | Sodium[b] | 37,500 | 120,000 |
| Arsenic[b] | <0.005 | 151 | Strontium[a] | – | 6200 |
| Barium[a] | ND | 26 | Sulfate[a] | <0.1 | 47 |
| Barium[b] | 9.65 | 1740 | Sulfate[b] | ND | 19 |
| Boron[a] | ND | 56 | Tin[a] | ND | 1.1 |
| Bromide[b] | 150 | 1149 | Zinc[a] | ND | 0.022 |
| Cadmium[a] | ND | 0.015 | Zinc[b] | <0.02 | 5 |
| Cadmium[b] | <0.02 | 1.21 | TOC[a] | 67 | 38,000 |
| Calcium[a] | ND | 25,000 | Surfactants[b] | 0.08 | 1200 |
| Calcium[b] | 9400 | 51,300 | Benzene[a] | 1.8 | 6.9 |
| Chloride[a] | 1400 | 190,000 | Benzene[c] | <0.010 | 10.3 |
| Chloride[b] | 81,500 | 167,448 | Toluene[a] | 0.857 | 3.37 |
| Chromium[a] | ND | 0.03 | Toluene[c] | <0.010 | 18 |
| Copper[a] | ND | 0.02 | Oil/grease[a] | 6 | 60 |
| Copper[b] | <0.02 | 5 | Oil/grease[b] | 2.3 | 38.8 |

[a] (Fillio et al. 1992) [b] (USEPA 2000) [c] (Shepherd et al. 1992)

## 1.8 Oilfield Produced Water Management

Over the economic life of a producing field, the volume of water can be more than 10 times the volume of hydrocarbon produced. According to the American Petroleum Institute, produced water is the largest waste-stream source in the exploration and production (E&P) industry and the goal of a water treatment facility is a higher quality stream of water that can be managed at the surface and a concentrated stream of wastewater that can be disposed through underground injection. Waste from E&P operations fall into four primary categories:

- Produced water : the saline water brought to the surface with oil and gas
- Drilling waste: the rock cuttings and fluids that are produced from drilling a new wellbore into the subsurface
- Associated wastes: a variety of small volume waste streams that encompasses all other types of wastes uniquely "associated" with oil and natural gas production
- Industrial wastes: these are the wastes that are not uniquely associated with oil and gas production that are nonetheless generated at well sites. Examples include paint, spent solvents and packaging materials.

# CHAPTER II

# LITERATURE REVIEW

## 2.1 Membrane Separation Process

A membrane process can be defined as a separation process where a feed stream containing pollutants that have to be removed, is split into a clean water stream also known as the permeate, and a concentrated stream called the concentrate. Membrane filtration technology is one of the newest and more advanced techniques in water treatment. It is a technology that is economical, environmentally friendly, versatile, and easy to use, making it a leading choice for water purification applications. Figure 2.1 is a schematic of the operating principle of membranes.

Membrane technology is widely accepted as a means of producing high purity water from surface water, well water, brackish water and seawater. Membranes are thin film barriers of synthetic organic or inorganic materials. They are used in industrial processes and wastewater treatment, as well as extensively in the pharmaceutical and food processing industries. The main attribute of membrane technology is the fact that it works without the addition of chemicals, with a relatively low energy utilization that is easy to use in a well-arranged process. Membranes play a primary role of acting as a selective barrier in the presence of a driving force allowing the passage of certain particles or components of the stream based usually on size (filtration) and the retention of the larger components of a mixture.

Membranes inadvertently act to enrich one of the streams i.e. the concentrate. Separation by membranes is not limited to particle separation but extends filtration to include the separation of dissolved solutes in liquid streams and separation of gas mixtures. Unlike a conventional filtration process, which operates in a "dead-end'' mode, many new industrial membranes are configured to be operated in a "cross-flow'' mode, where the feed is pumped tangentially over the surface of the membrane, resulting in two product streams.

Membranes are classified in many different ways, including describing them by the driving forces used for separating materials, that is, pressure, temperature, concentration, and electrical potential, mechanism of separation, the structure and chemical composition, and their geometry of construction. In water treatment, the membranes most widely used are pressure driven. When a pressure difference is applied over the membrane, the feed stream is partly forced through the membrane. This results in the removal of certain solutes, and the type of solutes that is removed depends on the pore size of the membrane. The clean water stream or permeate that is thus produced is the desired product stream in water treatment applications. However, the removal of the solutes results in an accumulation of these solutes on the feed side of the membrane, resulting in a concentrated stream that still has to be disposed of. This is one of the major shortcomings of membrane processes. Contaminants are not eliminated, but only separated from the product, and the concentrated stream cannot always be discharged to the environment. Each membrane process is best suited for a particular water treatment function, and must be carefully weighted for prior use in a given separation.

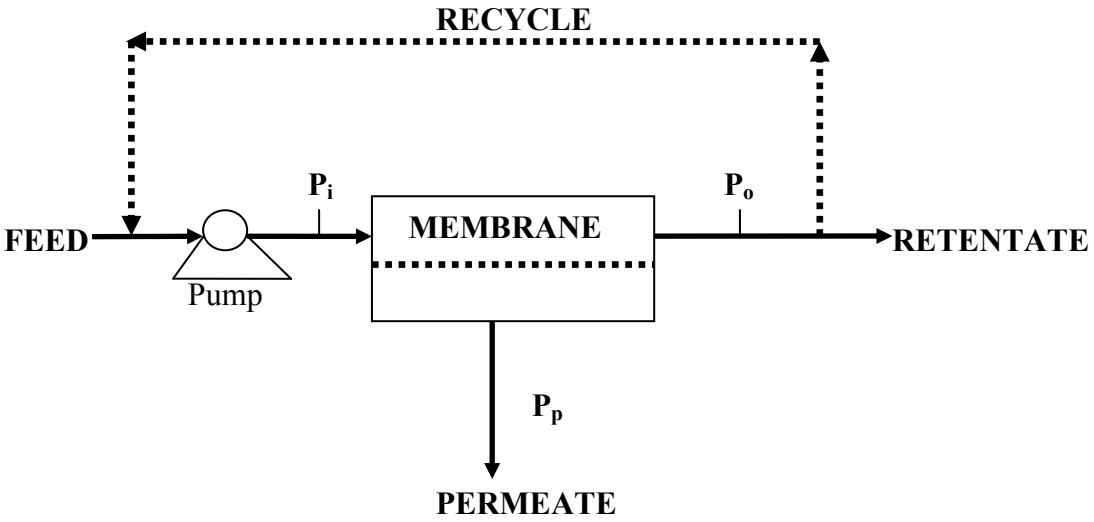


**Fig. 2.1—Operating Principle of Membrane Technology**

## 2.2 Membrane Characteristics and Types

According to the driving force that is used to produce the clean water, several membrane processes can be distinguished with each membrane process is best suited for a particular water treatment function. Driving forces in membrane separation processes are hydrostatic pressure, concentration and electrical potential differences. Depending on the assumed pore size of the membranes, four different pressure driven membrane processes can be distinguished. The membranes with the smallest pore size are called reverse osmosis membranes, and sometimes hyper fillers and can separate dissolved salts from water molecules. Therefore, they are often used for desalination of seawater. Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO), or Hyper filtration (HF) utilizes high pressures across the membranes to accomplish filtration of contaminants from the produced water. These technologies are the most common membrane techniques of water purification. The membranes also are

continuously being upgraded or modified for further improvement in performance and use.

MF, UF and NF are based on the principle of rejection of species greater than the pore size of the membrane under pressure. RO uses an operating pressure higher than the osmotic pressure of salt present in the water to drive pure water through the membrane, thereby rejecting the salts. It is reversal of the natural osmosis process where water flows from the higher concentration solution to the lower concentration solution to natural equilibrium. MF membranes are a low pressure process which separates suspended solids and bacteria from liquids and gases. UF membranes remove macromolecules such as proteins and polysaccharides, colloidal materials, and viruses from liquid streams.

NF membranes are designed to selectively remove multivalent ions rather than univalent ions, and they reject mechanistically on two levels. First, un-charged soluble organics are rejected based on size and shape. The molecules are too big to pass through the pores. The second level of selectivity is for charged soluble salts that are much smaller than the membrane pores. The tighter NF membranes, i.e. those with the smallest pore sizes are so selective and can fractionate or separate divalent (+2 charge) anions from monovalent (+1 charge) anions. RO membranes are used to remove salt from brackish and seawater solutions, and separate dissolved and ionic components. Their pore sizes are so small that they can be used to concentrate a variety of substances from antifreeze to wine. Figure 2.2 shows a schematic for membrane definition.

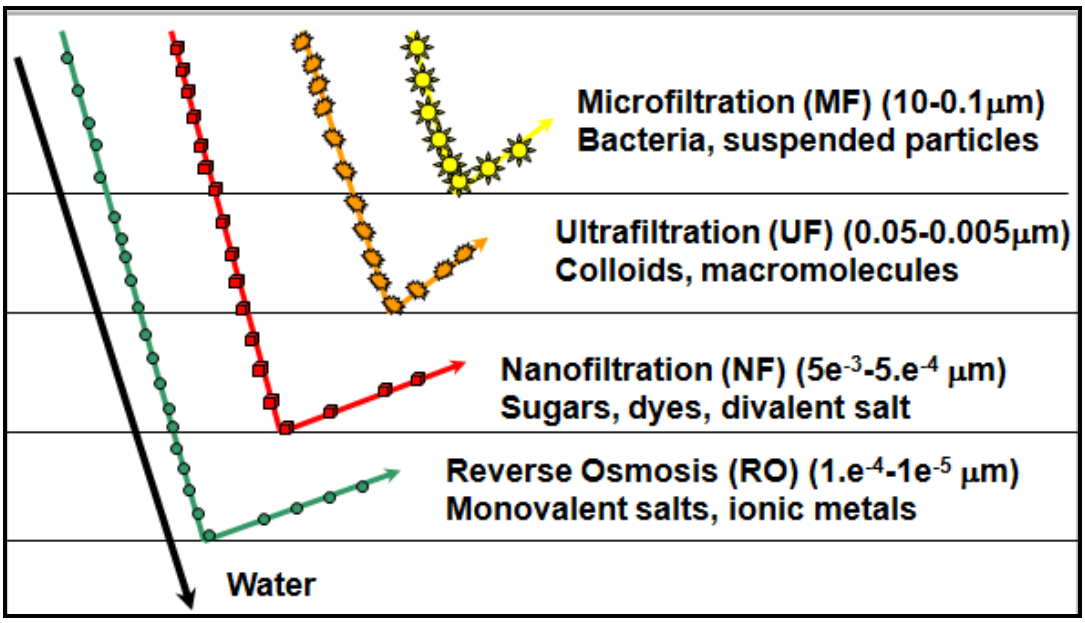


**Fig. 2.2— Definition of Membranes**

## 2.3 Membrane Chemistry and Materials

Materials used in membranes are polymers used in diary systems such as cellulose acetate, polyamide, polysulfone, etc. and inorganics uncommon in diary systems. Ceramic and stainless steel are examples of materials used in making inorganic membranes.

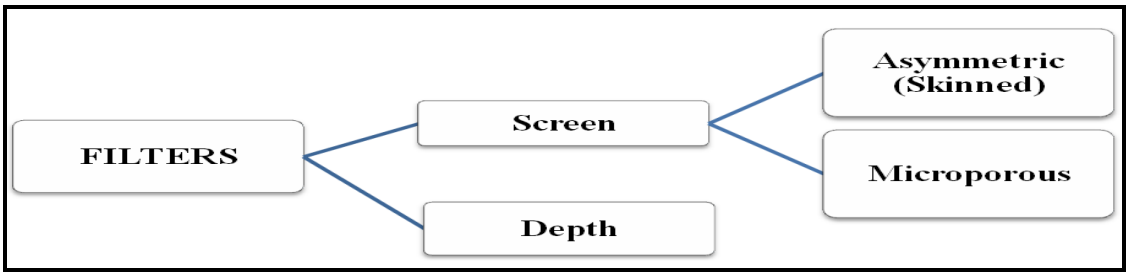


**Fig. 2.3— Membrane Classification**

Depth filters derive their names from the fact that filtration or particle removal occurs within the depth of the filter material. They consist of a matrix of randomly oriented fibers or beads bounded together to form a maze of flow channels. Common materials of construction include cotton, fiberglass, asbestos, sintered metals, and diatomaceous earth. Particles that are insoluble or collodial in nature are removed from a fluid by entrapment or adsorption to the filter matrix. A Screen filter separates by retaining particles on its surface and it has defined pore size. Membrane filters fall into the screen filter category. Screen filters are further classfied based on their ultrastructure into asymetric skinned membranes and microporous. Food and dairy products are examples of companies were membranes are used. Figure 2.3 shows membrane classification.

Microporous membranes are designed to retain all particles above their pore size ratings, while a asymmetric membrane is characterised by a thin skin on the surface of the membrane, rejection occurs only at the surface, and retained particles above the nominal molecular weight cut-off (MWCO) do not enter the main body of the membrane. MWCO is the ability of a membrane to reject the species of certain molecular weight given in Daltons (Cheryan, 1998).

Typically, MF membranes are made of polymeric materials, for the most part asymmetric. A list of commonly used polymers includes Teflon (PTFE), polyvinylidene fluoride (PVDF), cellulose acetate, polysulfone, nylon and polycarbonate. Non-polymeric submicron membranes manufactured from durable materials such as ceramics

and metals are used for MF separation. UF membranes are typically asymmetrical polymeric membranes like the MF membranes.

NF membranes were initially manufactured from asymmetric cellulose acetate, but now are more typically made of a thin-film composite polymeric base such as polysulfone cross linked and on its surface. RO membranes are typically asymmetric cellulose acetate or thin-film composite, with the most common thin-film being a polyamide film bonded to a submicron-pore-size polysulfone base.

### 2.3.1 Polymeric Membranes

Polymeric membranes are membranes of polymeric macromolecules composed of repeating structural units connected by covalent chemical bond interphases, which can selectively transfer certain chemical species over others. While polymeric membranes are generally cheaper than ceramic membranes, they cannot be used at elevated temperatures. It is pertinent to note that solubility parameters can limit certain applications. Cellulose acetate (CA) is a polymeric membrane in which cellulose is the raw material.

Cellulose acetate is prepared from cellulose by acetylation, that is, reaction with acetic anhydride, acetic acid and sulfuric acid. Cellulose acetate membranes are widely used for reverse osmosis and ultrafiltration applications. They have high hydrophilicity which is essential in minimizing membrane fouling, low production and manufacturing cost and they can be produced with a wide range of pore sizes. Disadvantages are narrow use temperature and pH ranges, low chemical resistance and their tendency to biodegrade.

### 2.3.2 Polysulfone Membranes

This type of membrane is widely applicable for RO processes and highly useful due to its favorable material properties. The diphenylene sulfone repeating units in the molecule structure make the membrane strong and creep resistant. Characteristics such as a wide pH (1<pH<13) and temperature tolerance, max of 125$^{o}$C, resistance to chlorine, manufacturing ease, and the availability of a variety of pore sizes attribute to the membrane material being one of the most common used in RO processes. One disadvantage of this membrane is its susceptibility to fouling due to the hydrophobic nature of the polysulfone membrane surface interacting with several solutes and organic compounds (Cheryan, 1998).

### 2.3.3 Polyamide Membranes

These membranes have repeating amide bond in their molecular structure hence their name. They have better pH tolerance than cellulose acetate membranes and can withstand high pressures. A major drawback of these membranes is their vulnerability to chlorine degradation and biofouling tendencies (Cheryan, 1998).

### 2.3.4 Inorganic Membranes

They are also known as ceramic or mineral membranes. They are made from a wide range of inorganic artificial or synthetic materials. The common ones are made from alumina, titanium, and zirconia and silicon oxides. In their manufacture they are often formed into asymmetric, multi-channel elements and normally have an

asymmetrical structure composed of at least two, mostly three, different porosity levels. They are a vast improvement both in material characteristics and in the technology dividend to membrane filtration over polymeric membranes. They are inert to common chemicals and solvents, can withstand high acidity and alkalinity, operate at elevated temperatures, pH, and pressure limits, and they have long life and good durability. Limitations common to them include brittleness, relatively large energy consumption in operating them and pore size limitation in the lower micron range.

## 2.4 Membrane Configurations

This concept refers to the packing of the membrane in the module so that it can be installed in a system. Common configurations include plate and frame, tubular, spiral-wound and hollow fiber.

### 2.4.1 Plate and Frame Module

The plate and frame membrane configuration consist of sheets of membrane placed between plates. In between the plate and one surface of the membrane is a net like material known as a scrim which provides a channel for permeate to flow. The plates are sealed together, while allowing a method for the removal of the reject. Plate and frame membrane configuration are not commonly used for municipal water treatment but are more appropriate for certain waste or food processing applications where there is a high fouling tendency.

Advantages in using this configuration include ease in membrane replacement and intermediate operating conditions involved in terms of energy consumption, packing

density and hold-up volume. Labor and hardware required in its operation are major disadvantages. Plate and frame configurations are shown below in Figures 2.4 and 2.5.

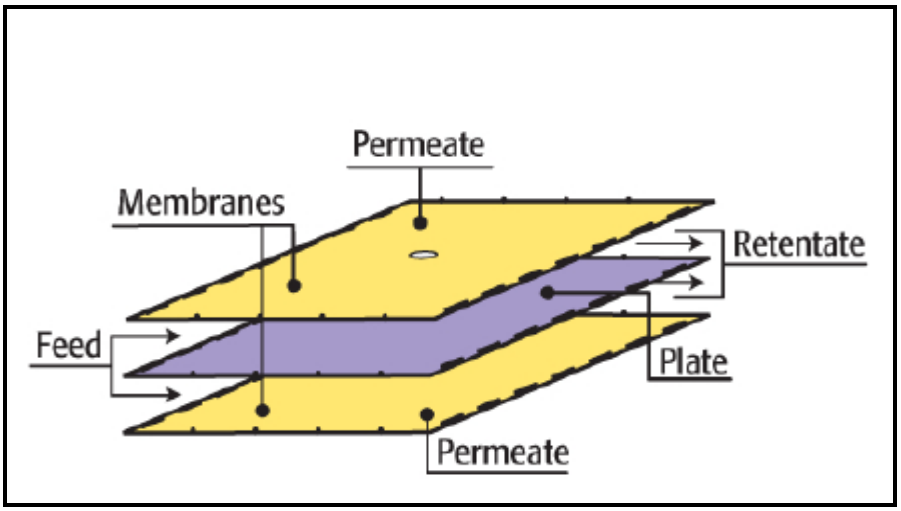


**Fig. 2.4—Cross Section of Plate and Frame Membrane Configuration (Source: www.cdr.wisc.edu)**

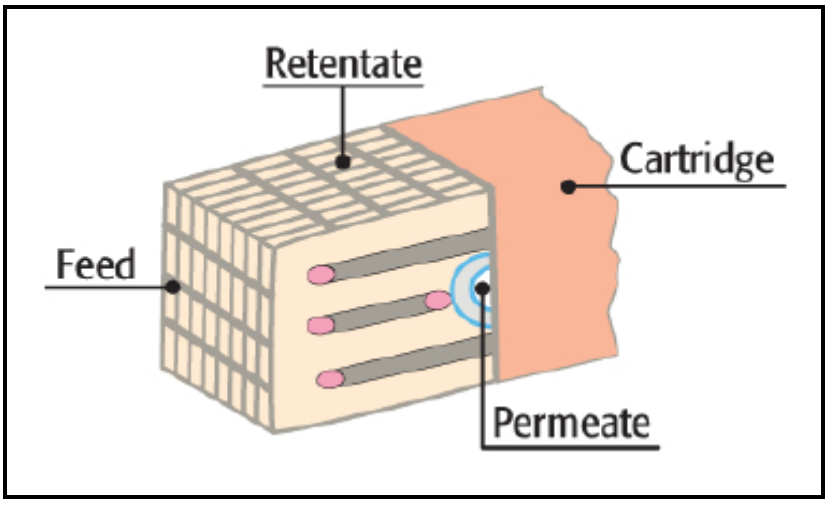


**Fig. 2.5—Cassette Design of Plate and Frame Membrane Module (Source: www.cdr.wisc.edu)**

### 2.4.2 Spiral-Wound Membrane Configuration

Spirally wound modules are constructed from flat sheets of membrane glued back to back on three sides forming an envelope around a porous support material. The open end of the membrane envelope is attached around a tube with holes which provide a route for permeate to flow out. The membrane is wound up around the centre tube to form a cylindrical element. Water that has passed through the membrane in service flows towards the centre tube through the porous support. The rolled up membrane leaves are separated by a mesh spacer, which also serves to promote turbulence in the feed channels. These membrane modules are chiefly designed for cross flow use, with the feed stream running mostly parallel to the membrane surface. Advantages of this configuration includes high packing density, easily replacement of membranes, low pressure drops, lower capital costs and lower energy utilization. Difficulty in cleaning when heavily fouled, intolerant to pressure differences, and membranes being easily clogged by particles are disadvantages of this configuration. Figures 2.6 and 2.7 shows Spiral-wound membrane configurations and its cross-section respectively.

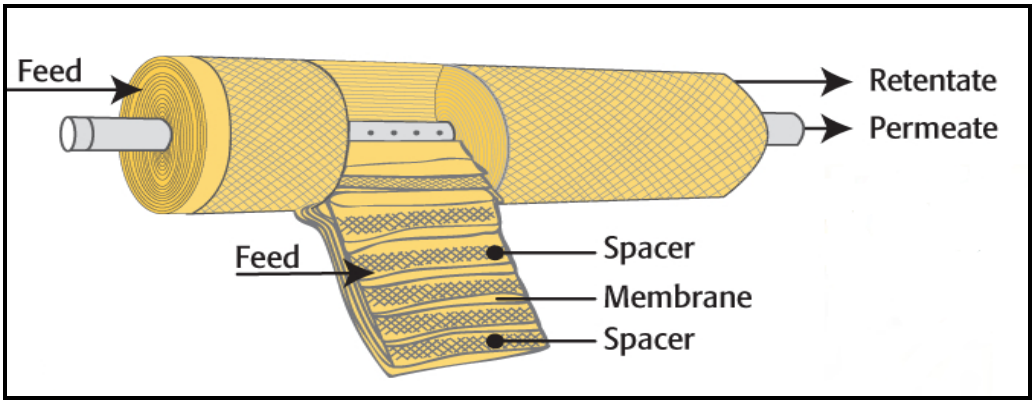


**Fig. 2.6—Spiral-Wound Membrane Configuration**

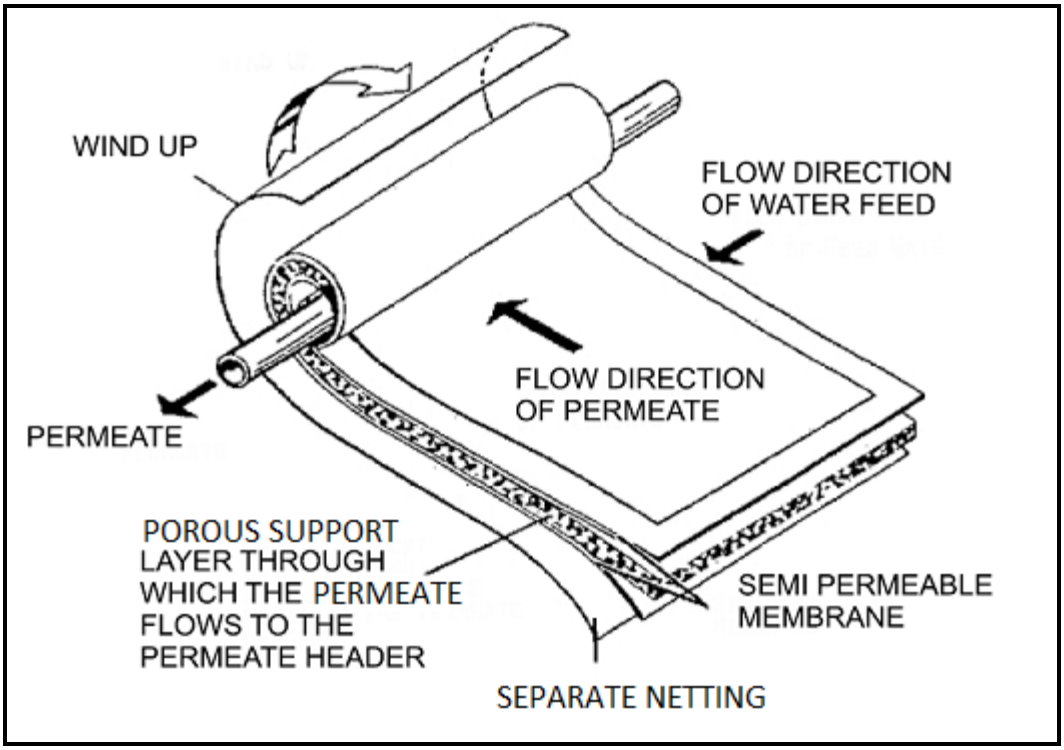


**Fig. 2.7—Membrane Cross Section**

### 2.4.3 Tubular Membrane Configuration

Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. The membrane is cast on the inside surface of a porous tube. The feed solution is pumped through the center of the tube at velocities as high as 20 ft/sec. These cross-flow velocities minimize the formation of a concentration polarization layer on the membrane surface, promoting high and stable flux and easy cleaning, especially when the objective is to achieve high suspended solids in concentrate. Permeate is driven through the membrane to be directed out of the system or back into the process depending on the application. It has several tubes (3 to 19) per housing.

Tubular membranes are based on either PVDF (polyvinylidene fluoride) or PS (polysulfone). They are capable of continuous, reproducible processing cycles, which means they are cleanable, durable, easy to operate and a proven advance in technology. Large space requirement, high hold up volume, and highest use of polymeric type systems because of substantial pressure drops are disadvantages of this kind of module. Figure 2.8 is a tubular membrane module.

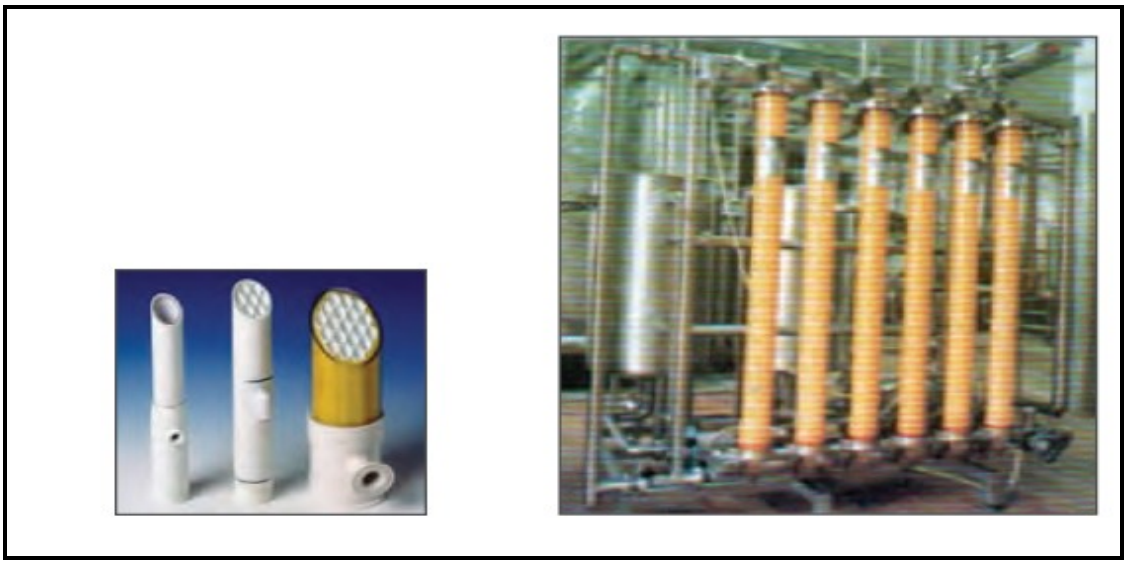

**Fig. 2.8—Tubular Membrane Module**

2.4.4 Hollow Fiber Membrane Configuration

The hollow fiber configuration describes membranes which are cast as fine tubes or lumens. This membrane configuration offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation.

The hollow fiber geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption. They represent the latest of all membrane modules and have a high surface to volume ratio. Disadvantages are that this module is intolerant to large pressure changes and are readily plugged by particles. Figure 2.9 is a picture of the hollow fiber membrane module.

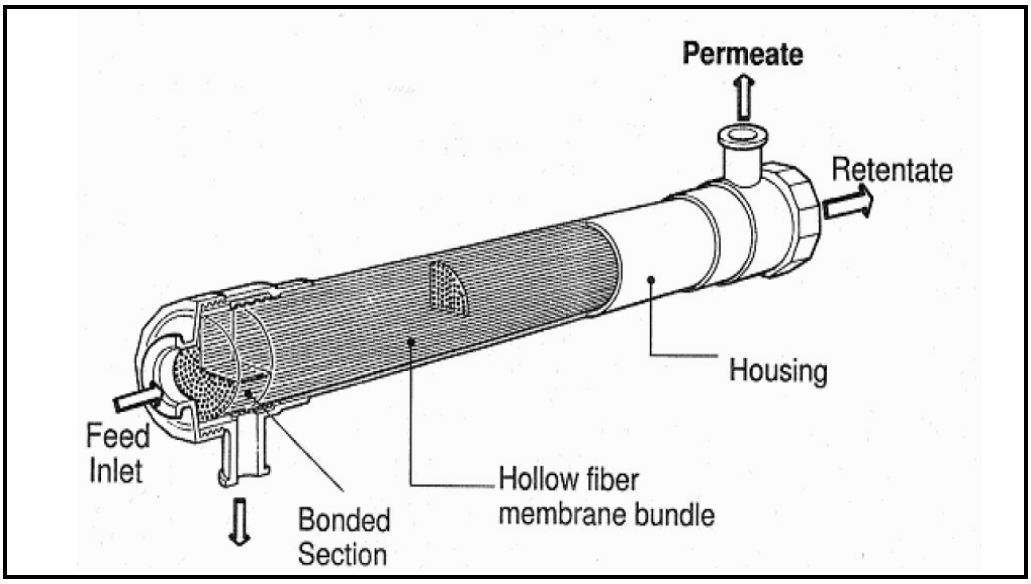


**Fig. 2.9—Hollow Fiber Membrane Module**

## 2.5 Membrane Fouling

Membrane performances may be difficult to predict and may not remain constant with time due to two phenomena called concentration polarization and fouling. Concentration polarization is the build-up of solutes and the formation of a gel layer on membrane surface. The increased resistance of the gel layer results in lower flux.

Concentration polarization effects are affected by operating parameters such as crossflow velocity, pressure, temperature, and feed concentration.

Fouling is a process in which the membrane absorbs or interacts with solutes in the feed stream. It is an undesirable formation of deposits on the surface of the membrane and consequent reduction of flux and membrane selectivity. Fouling occurs when the rejected solids are not transported from the surface of the membrane back to the bulk stream. As a result, dissolved salts, suspended solids and microorganisms accumulate at the membrane surface. Fouling is usually an irreversible and time dependent process and it occurs during an increase in transmembrane pressure to maintain a particular water flux or during a decrease in water flux when the system is operated at constant pressure. The following processes are the main causes of fouling:

- Inorganic deposits (scaling)
- Organic molecule adsorption (organic fouling)
- Particle deposition (colloidal fouling)
- Microbial adhesion and growth (bio-fouling)

Fouling decreases the performance of membranes. To reduce the problem of fouling, the feed water can be pretreated and in addition, chemical cleaning and periodic backwashing may be required to restore membrane performances. Typically reducing the operating flux and recovery will reduce fouling. Effects of membrane fouling include:

- Increased cleaning and maintenance cost of the membrane system.
- Deterioration in the product water quality (permeate quality) i.e. increase in the passage of dissolved materials (salts) in permeate (decreased salt rejection).

- Decline in flux with time.
- Decrease in rejection of solutes.
- Increase in transmembrane (feed pressure) and differential pressure with time.
- Reduced membrane life.

## 2.6 Operating Parameters of a Membrane

During membrane filtration, certain operating parameters are required in describing the mechanism of separation and transport through the membrane and measuring if filtration is feasible in order to determine methods of improving filtration. For the purpose of treating produced water and achieving objectives such as suspended solids removal and volume reduction, the following parameters are essential.

**FLUX (J)** is the flowrate through the membrane. It is also the quantity of solution that passes through a unit of membrane area in a given amount of time. The idea is to use minimal membrane area to produce larger permeate flux, this saves on energy and space and brings good economic return on filtration. Flux can be calculated in liters per $m^2$ per hour (LMH). Flux is mathematically defined by the following equation:

$$\text{Flux} = \frac{\text{Volume of permeate}}{\text{Membrane area} * \text{Time}} = \frac{\text{Liters}}{m^2 * h}$$

Pure water flux ($J_w$) differs from the permeate flux as it measures the permeate flux using RO water as the feed under specified conditions of temperature, pressure and cross flow velocity, it is an essential measurement in membrane fouling studies.

**REJECTION RATE (R)** is when pressure is applied to water in contact with a membrane, water passes through the membrane and the solids in the water are rejected.

The degree to which the solids are repelled is the rejection rate. The overall rejection rate depends upon the average concentration of dissolved solids in the feed as given below:

$$\% \text{ Rejection} = \left(1 - \frac{\text{Permeate concentration}}{\text{feed concentration}}\right) * 100$$

R = 100% when permeate concentration = 0

R = 0% when permeate concentration = feed concentration

**CROSS-FLOW VELOCITY** is the velocity of flow across the membrane surface. It is a function of pressure.

$$\text{Cross} - \text{flow velocity} = \frac{\text{cross flowrate}}{\text{cross} - \text{sectional area}} = f(\Delta P)$$

$$\text{Energy consumption} = \text{flowrate} * \Delta P$$

**RECOVERY** is the percentage of the feed flow that passes through the membrane and becomes the permeate stream. It is an estimation of the performance of a membrane system. It measures the volumetric fraction of permeate to the feed showing how much of permeate is recovered from the feed. It is also called separation efficiency.

$$\% \text{ Recovery} = \frac{\text{Permeate volume}}{\text{Initial feed volume}} * 100$$

**CONCENTRATION FACTOR (CF)** quantifies the effect of system recovery on the concentration of the rejected contaminants in a membrane operating system.

$$\text{Concentration factor} = \frac{1}{1 - \text{recovery}}$$

Concentration factor is as a result of a mass balance and it is based on the assumption that the membrane provides complete rejection of the contaminant in the water.

**TRANSMEMBRANE PRESSURE (TMP)** is the force which drives liquid through a crossflow membrane. TMP is calculated as an average related to the pressures of the inlet, outlet and permeate ports. It is expressed as:

$$\text{TMP} = \left(\frac{\text{feed pressure} + \text{concentrate pressure}}{2}\right) - \text{permeate pressure}$$

Since the crossflow gives rise to a pressure drop from the inlet to the outlet of the membrane module as shown in figure 2.1 earlier, the feed-side pressure is given as:

$$\text{Feed} - \text{side pressure} = \left(\frac{\text{inlet pressure} + \text{outlet pressure}}{2}\right)$$

**Assumptions:**

- Steady state conditions, i.e., flow is independent of time
- End effects are negligible
- Density is constant i.e. the liquid is incompressible
- Flow through the pores is laminar, Re < 2100

**pH and Conductivity**: these two parameters are measured with standard equipment during membrane filtration.

# CHAPTER III

# EXPERIMENTAL PROCEDURE

## 3.1 Process Train for Produced Water Treatment

Barrufet et al. (2005) investigated and concluded that the general approach for produced water treatment is de-oiling and demineralizing before disposal or reuse. Treatment options for produced water consists of removing the suspended oil and grease (hydrocarbons), dissolved hydrocarbons (BTEX, VOC, etc.), suspended solids, macromolecules, polymers, bacteria, and other contaminants, and finally the removal of salts from the produced water by membrane desalination. A rule of thumb in this work is that produced water must be pretreated before subsequent treatment with membranes. Pretreatment methods available for the removal of suspended solids from water before it is processed through membranes include back washable filters, bag filters, depth filters, media filters, screens and strainers.

## 3.2 Proposed System

The method deployed consists of pretreating produced water with a media filter for primary removal of larger suspended hydrocarbon particles followed by passing it through an oil removal cartridge filter for removal of suspended solids and dissolved oil and grease (hydrocarbons). The pretreated produced water is then passed through a microfiltration membrane to further remove larger suspended solids. Ultrafiltration is employed if necessary. Otherwise multivalent ions are then removed from the produced water using nanofiltration desalination membranes.

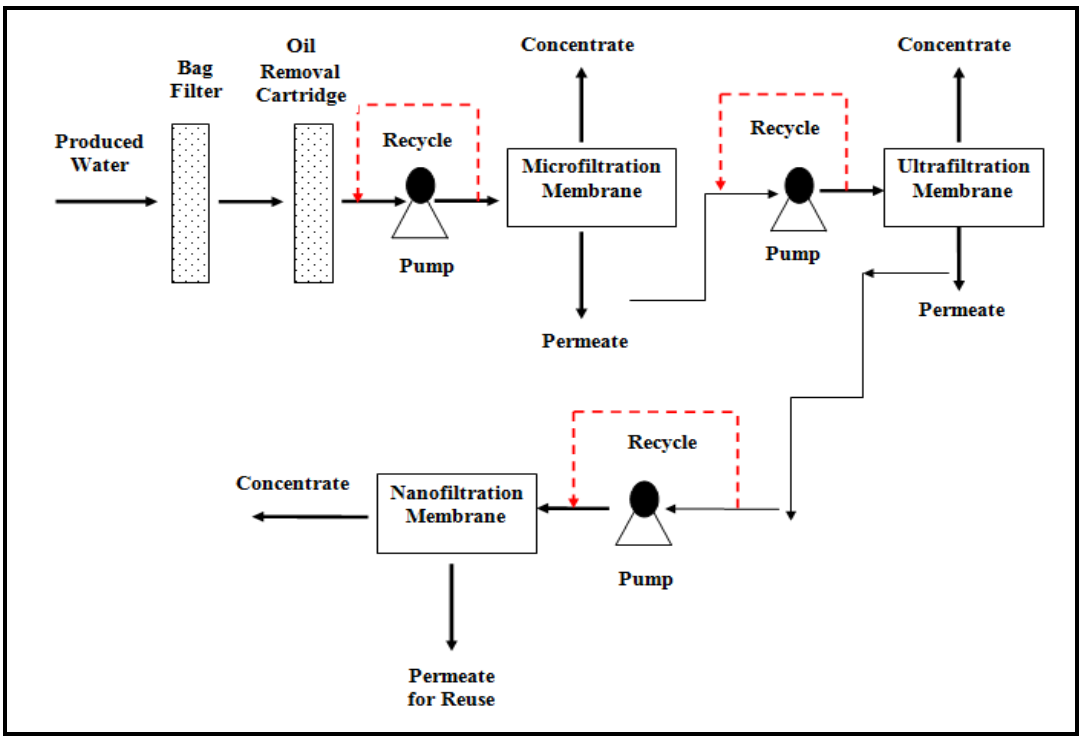


**Fig. 3.1—Process Train for the Treatment of Oilfield Produced Water**

## 3.3 Description of the Process Train

The filtration components tested in the process train are as shown in Figure 3.2. Oil removal was achieved using Mycelx or Polymer Ventures filter cartridges. Microfilters in hollow fiber, ceramic and flat sheet configurations were used to remove large particles and total suspended solids, while flat sheet nanofilters were used to achieve water softening. Reverse Osmosis membranes and the chemical cleaning system were not evaluated during the pilot tests.

Figure 3.2 also shows the analytical tests done in each stage of the process train and these were used to evaluate the effectiveness of each process in the train.

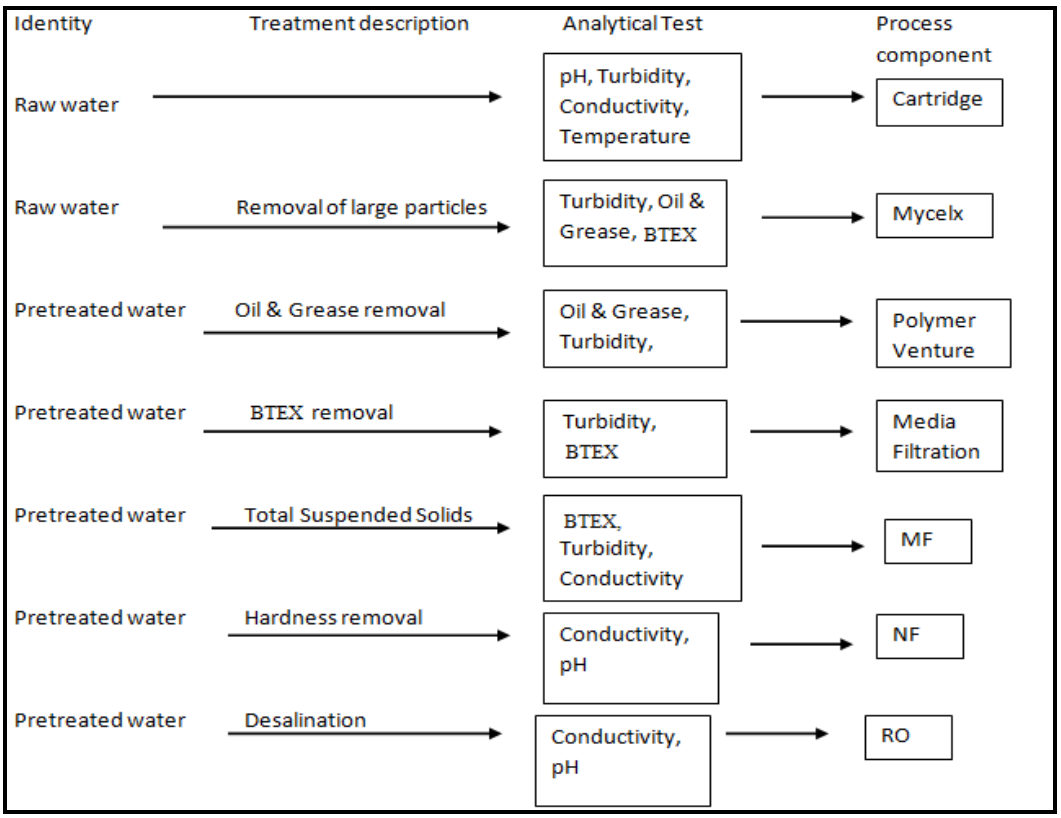


**Fig. 3.2— Schematic of the Process Train**

## 3.4 Modular Components and Experimental Set Up

The GE Sepa CF II Med/High System manufactured by GE Osmonics was used for a series of tests with flat sheet membranes. It is a crossflow membrane filtration unit and the cell has an effective membrane area of 155 $cm^2$, 70 ml hold up volume and a maximum operating pressure of 1000 psi. This lab scale crossflow membrane filtration unit provides fast and accurate performance data with small lab scale features such as cost, time, and membrane surface area. Its design simulates the flow dynamics of full scale operation.

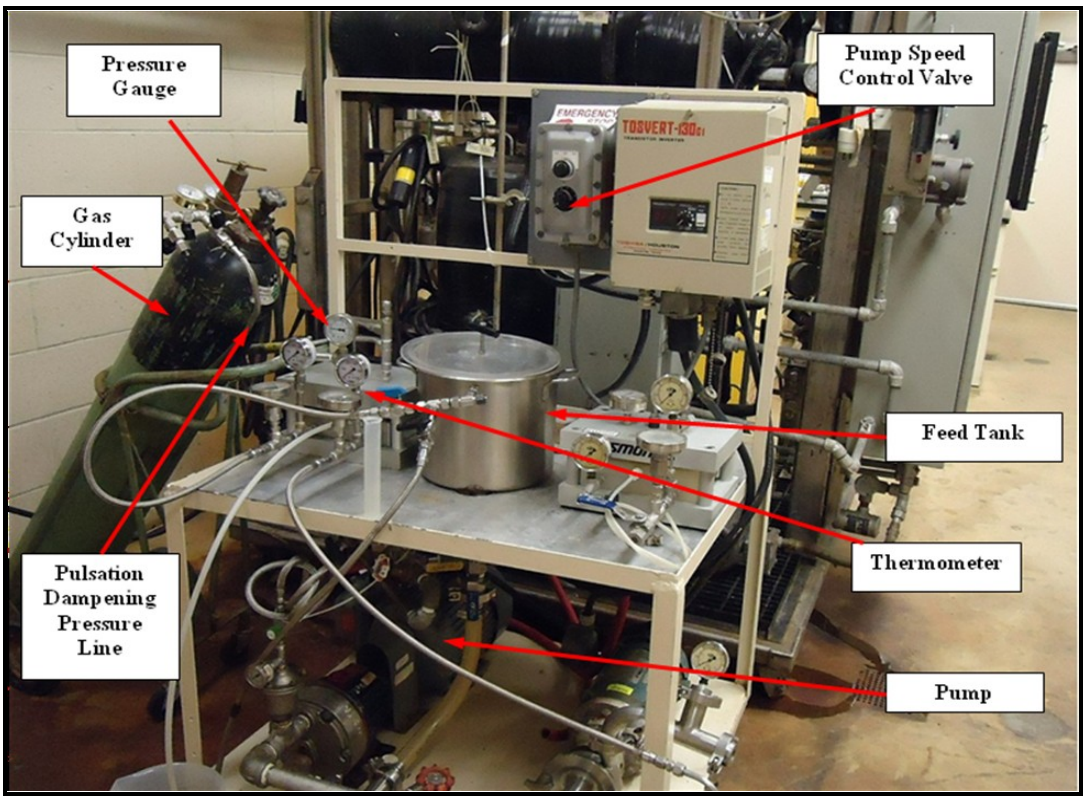


**Fig 3.3—Pilot Plant Flat Sheet Membrane Unit Set Up**

The system was operated at total recycle mode, permeate was recycled to ensure that all membranes were exposed to the same concentration of suspended solids, regardless of the permeate flux of each membrane. With membrane inserted into the cell, pressure is used to achieve perfect sealing of the cell. The unit was operated by pumping feed from the feed tank through the system. Pressure is applied on the cell using a compressed nitrogen gas from a gas cylinder and maintained by adjusting a pressure relief valve located at the concentrate outlet pressure gauge.

In order to prevent pulsation while running a test, pressure was added to the pump outlet to dampen the pressure fluctuation between the suction and driving forces.

This is maintained by opening and closing a valve located on the tube going from the gas cylinder to the dampener. The apparatus for this test are shown in Figures 3.3 and 3.4.

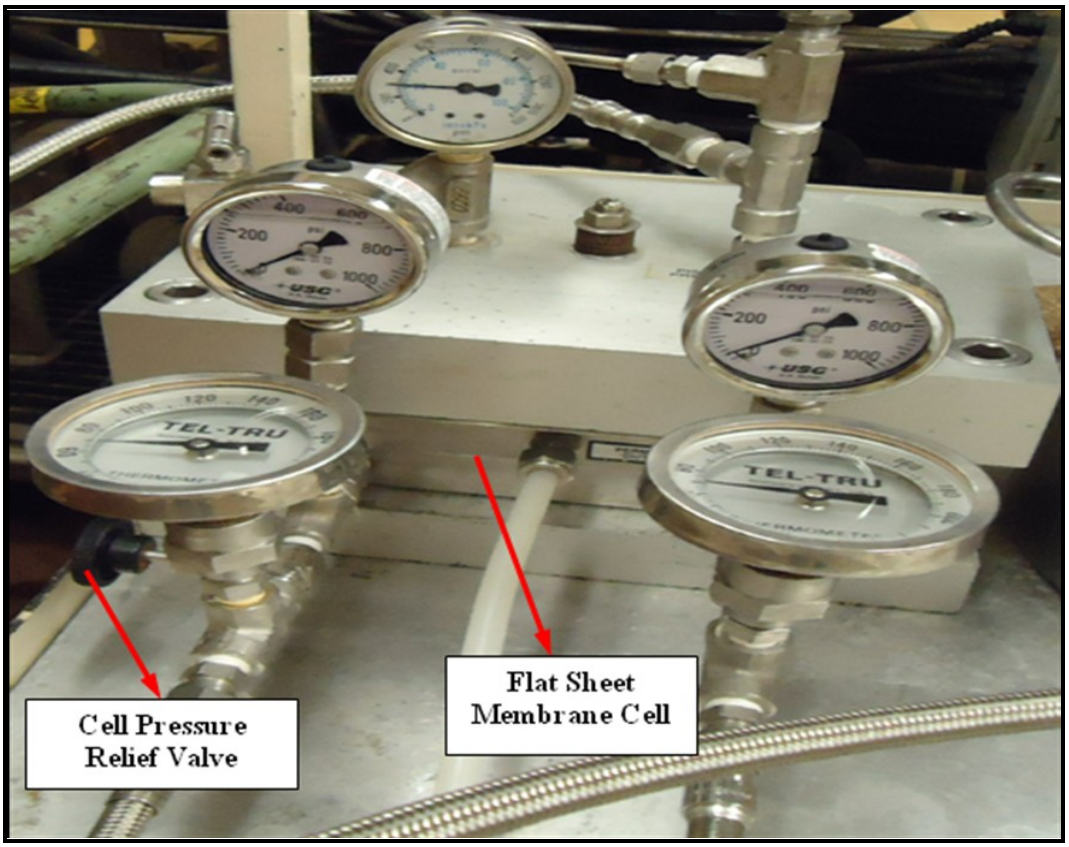


**Fig. 3.4—GE Osmonics Sepa Cell**

While the test was being performed, pressure, temperature, and flux around the membrane are measured and recorded. A baseline test is done with reverse osmosis water before and after testing with oilfield brine in order to establish an efficiency and flux pattern of the used membrane. For other membrane configurations such as hollow fiber, ceramic, etc, a retrofitted unit as shown in Figure 3.5 was used to perform pilot tests.

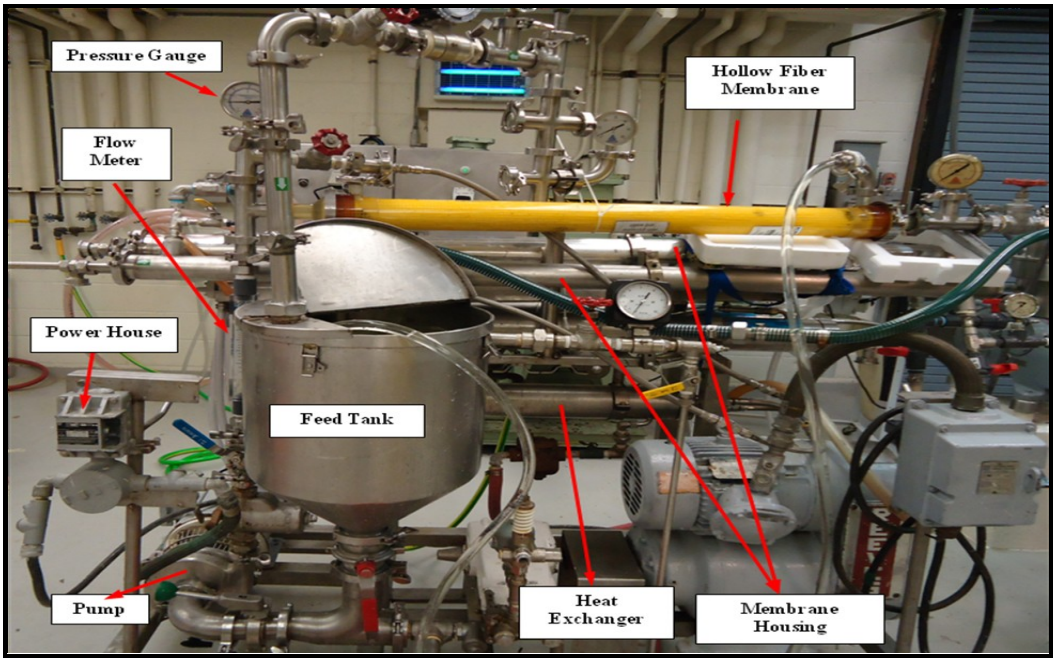


**Fig. 3.5—Pilot Plant Hollow Fiber, Tubular and Ceramic Membrane Configuration Unit**

The pilot plant unit shown in figure 3.5 above is a retrofitted unit made by the separation sciences department in Texas A&M. It has the capacity to handle three membrane configurations e.g. hollow fiber, ceramic, or tubular in parallel, although only one membrane housing connection was used for the purpose of this work. Before the start of any test, integrity tests were carried out to make sure there were no leaks in the unit as confirmed by pressure monitoring.

The feed tank contains the oilfield produced water to be purified, and which is then pumped through the membrane filters by a 5 horsepower centrifugal pump. A flowmeter is used to monitor the flow through the membrane from the feed outlet, while pressure gauges measure the inlet and outlet pressure across the membrane and a valve is used to control the flow rate from the pump. Permeate samples are collected through a

hose from the membrane outlet and the volumes are recorded. Temperature is maintained by passing cooling water through a heat exchanger across the system while pumping and treating the produced water and thermometer is used to read the sample temperature.

## 3.5 TAMU Mobile Treatment Unit (Field Testing Unit)

With the pilot test results from this research and past tests done, Texas A&M University in collaboration with the Global Petroleum Research Institute (GPRI), built a mobile membrane treatment unit for field testing of treating frac flowback and oilfield produced water. The membrane performance was validated in small scale pilot testing in the laboratory as well as through tests in field environments. The approach was to select a membrane capable of combining the properties of high flux separation efficiency, high tolerance for solids and fluid types, effluent solids and hydrocarbon removal.

## 3.6 TAMU Mobile Treatment Unit Capacities

- Bench top membrane efficacy test
- Oil removal testing
- Total suspended solids removal
- Total dissolved solids removal
- Membrane cleaning
- Analytical monitoring


**Fig. 3.6—TAMU- GPRI Mobile Treatment Trailer**

**Fig. 3.7—Interior of the TAMU- GPRI Mobile Treatment Trailer**

## 3.7 Details of the Mobile Treatment Unit

- Trailer skid mounted
- Capability:1,500 – 3,000 gal/day (≈ 1 -2 gpm)
- Power requirement: 220 volts; 5 hp motor
- Ability to operate unattended
- Weekly scheduled servicing
- Contains prefiltration conditioning unit, membrane filters, membrane filter polishing unit and online remote sensor monitoring water storage

# CHAPTER IV

# RESULT AND DISCUSSION

## 4.1 Oil and Organic Components Removal from Produced Water

This work used three media filters namely cartridge, Mycelx Inc. and Polymer Venture filters as process components to evaluate the effectiveness of oil and grease removal in the produced water. This treatment was aimed at removing free oil, dispersed droplets of crude oil, residual treating chemicals, and emulsified oil in the produced water. EPA's limitation for oil and grease discharge in produced water must meet both a daily maximum of 42 mg/L and a monthly average of 29 mg/L for offshore subcategory. The Striper sub-category covers wells that are located onshore and the oil and grease concentration is limited to a monthly average of 25 mg/L and a maximum of 35 mg/L. The removal method for oil and grease depends on the end usage of treated water and composition of oil in the produced water.

Oil is the primary organic material that is dispersed or dissolved in produced water at the time of discharge. Dispersed oil consists of small discrete droplets suspended in the water, while dissolved or soluble oil is present in dissolved form. Oil removal or organics removal has been investigated using various technologies such as carbonaceous absorbent (Gallup et al., 1996), bioreactors (Tellez et al., 2002), wetland treatment (Ji et al., 2002), ultrafiltration (Bilstad and Espedal, 1996), and nanofiltration (Dyke and Bartels, 1990).

Hydrocarbons that occur naturally in produced water include organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols, and volatiles. Organic components that are very soluble in produced water consist of low molecular weight (C2-C5) carboxylic acids (fatty acids), ketones, and alcohols. They include acetic and propanoic acid, acetone, and methanol. Partially soluble components include medium to higher molecular weight hydrocarbons (C6-C15). They are soluble in water at low concentrations, but are not as soluble as lower molecular weight hydrocarbons. These studies have given varying results for oil content removal.

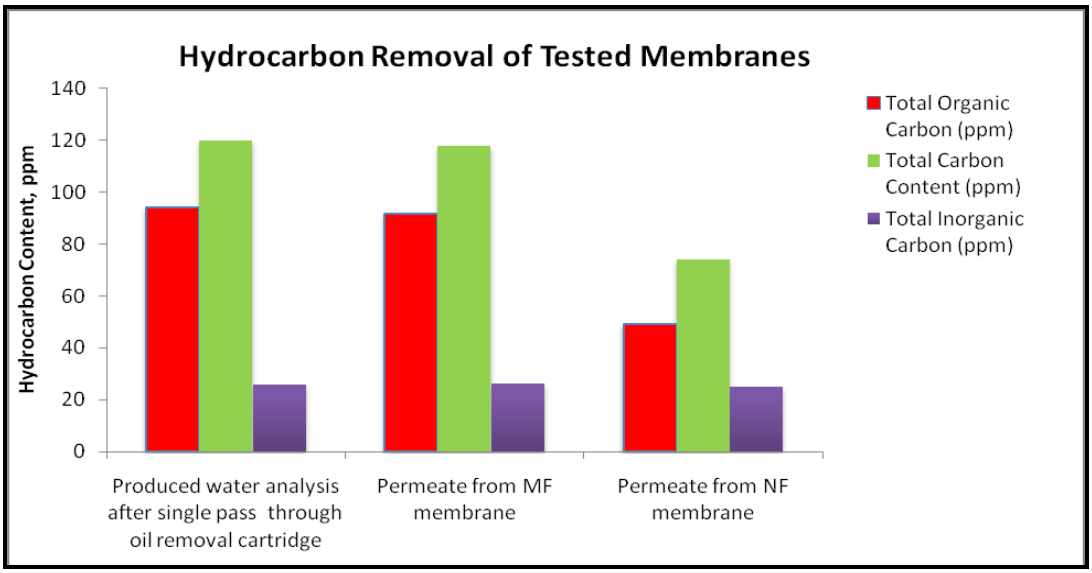


**Fig. 4.1—Total Organic Carbon Removal of Sampled Produced Water**

Fig. 4.1 above shows the results of a three step filtration process conducted on an oilfield produced water sample. The water was sourced at a disposal well site operated by Advanced Hydrocarbon located near College Station, Texas. The first step in treatment was filtration with 10 micron oil cartridge filter. It was used to remove large

diameter suspended solids and hydrocarbon. The second step was a 0.2 micron ceramic MF low pressure filter. This filter resulted in a reduction in turbidity but did not change the total dissolved solids (TDS) or ion content of the water. The MF filter did not significantly change the organic content of the water as evidenced by the Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC) levels. The third step was an NF membrane that showed a reduction in Total Dissolved Solids (TDS) and also significant reduction in both anionic and cationic species. While the TIC value remained the same, the TOC value was reduced. The TIC shows level that inorganic carbon in form of hydrocarbons or carbonates was not affected by this filter.

It can be seen from Fig. 4.1 that 47.9 % rejection of total organic carbon, and 37.3 % rejection of total carbon content and 3.66 % rejection of total inorganic carbon were achieved. Results were obtained from feed and permeate samples sent to a private laboratory for oil and hydrocarbon analyses. Measurements of Total Organic Carbon (TOC), Total Petroleum Hydrocarbon (TPH), Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) and Total Oil and Grease (TOGA) were reported. Each measurement type represents a portion of the organic content in the sample and will be sensitive to different classes of organics as follow:

- BTEX (SW 8260B) : volatile aromatic hydrocarbons - Extended
- TPH (EPA[1] 418.1): hydrocarbons
- TOG (EPA 413.2): hydrocarbons, alcohols, phenols, ketones, aldehydes

[1] Environmental Protection Agency

- TOGA (EPA 413.2): hydrocarbons, alcohols, phenols, ketones, aldehydes, C5+ organic acids

Another treatment for BTEX removal from oilfield produced brine was conducted using Mycelx filters, Polymer Venture filters, and Los Alamos National Lab (LANL) surfactant modified zeolite (SMZ) oil absorbent membranes respectively in combination to reduce the organic carbon content of the water prior to treatment with MF and NF. The chemical analysis of the treated permeated is shown in Fig. 4.2. The total BTEX removal from pretreatment to Mycelx cartridge filter[2] was 0.98%, Polymer Venture filter[3] cartridge was 0.99%, and reduction from a range of 46.8% to 52.7% for SMZ absorbent membrane.

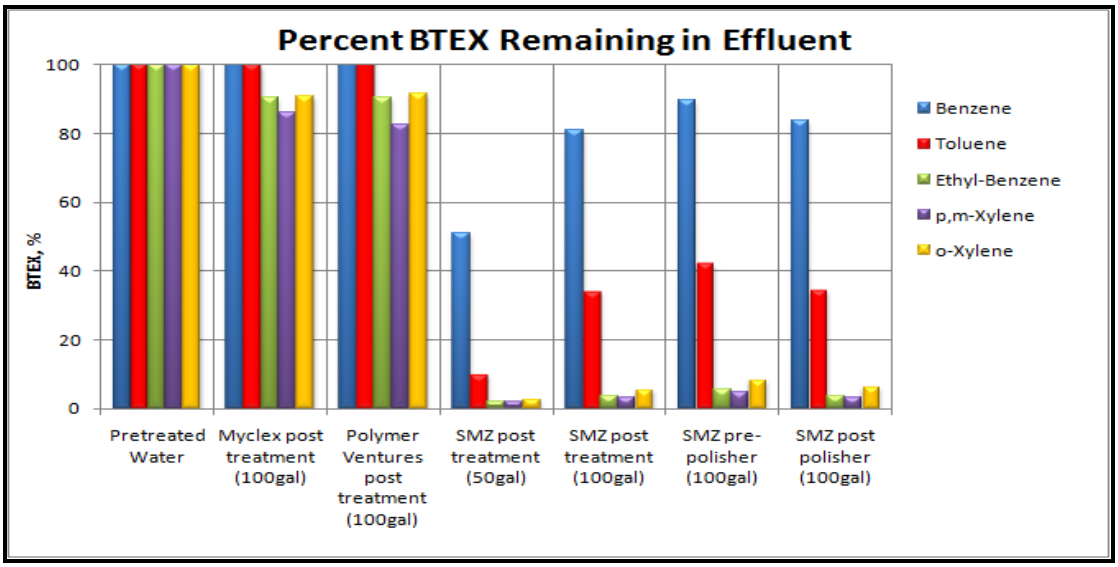


**Fig. 4.2—BTEX Removal Separation Efficiency**

[2] Mycelx Technologies Corporation

[3] Polymer Ventures Inc.

Figure 4.3 is a BTEX and oil and grease removal efficiency graph for permeate from a pretreatment with MF membranes. This was done to investigate separation efficiency of BTEX and oil and grease removal from MF after closed-cycle pretreatment prior to treating with an NF membrane. Table 1.3 shows the oil and grease content of raw water as 19.5mg/L and was not detected at the reporting limit after treating only 10 gallons of raw water. This indicates a 100% removal efficiency of oil and grease from this water sample.

**Table 1.3—Oil and Grease Removal Through Microfilter**

| | | |
|---|---|---|
| Raw Water | 19.5 | mg/L |
| 10 gallons flow(MF) | ND | Not detected at the reporting limit |

Figure 4.3 shows the BTEX removal efficiency from the microfilter. The overall BTEX removal efficiency was greater than 92% after treatment of 25 gallons water volume. Fig. 4.4 shows the percentage removal of BTEX after the treatment of 25 gallons of water volume.

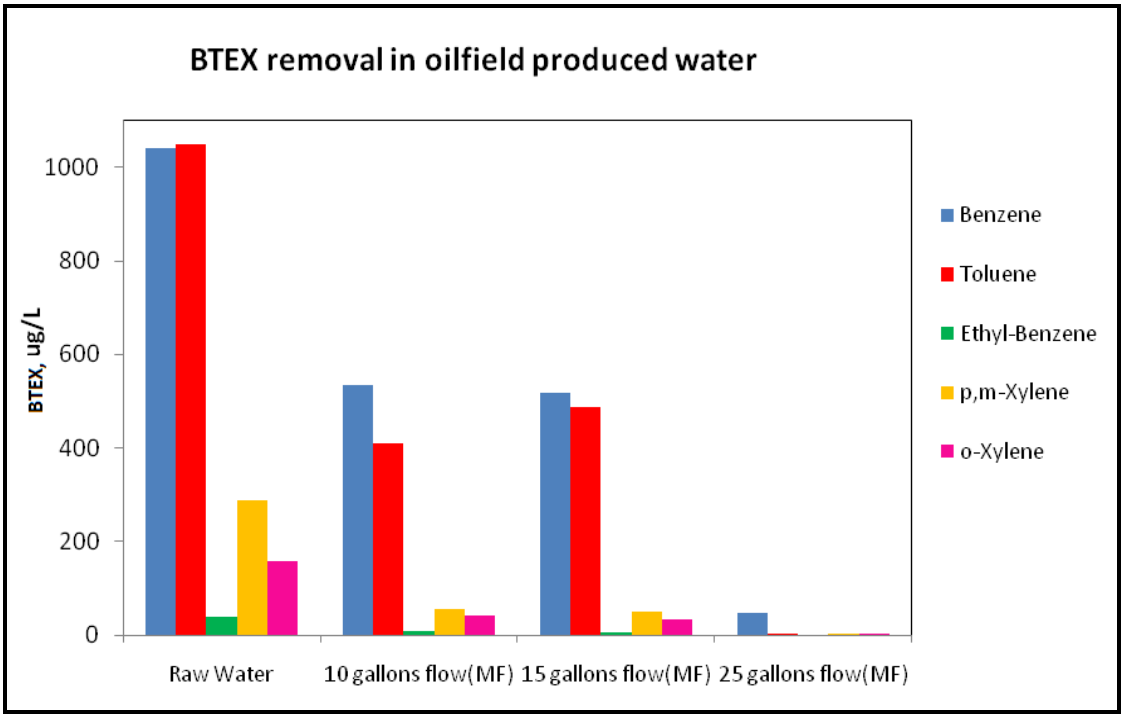


**Fig. 4.3—BTEX Concentration Removal for Tested Microfilter**

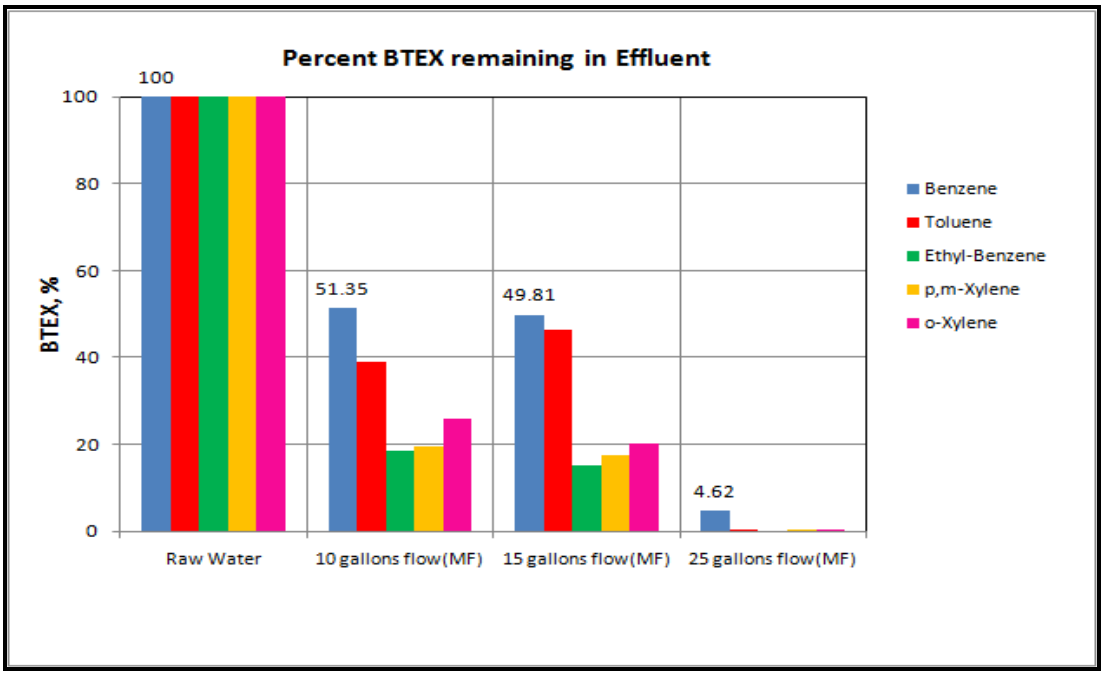


**Fig. 4.4—BTEX Removal Efficiency for Tested Microfilter**

## 4.2 Total Suspended Solid Removal Efficiency

For suspended solids removal, some form of filtration is the typical method used in industry. The concern with using filtration technology to remove the suspended solids from oilfield brine is the need to replace standard filters frequently if the water source has a high concentration of suspended solids. (Arthur et al., 2008) cited other techniques that have been tested for produced water suspended solids treatment such as activated carbon, ceramic microfiltration, and ceramic ultrafiltration.

Inadequate solids removal in water is a primary cause for further treatment failure. In this process train, cross flow microfiltration was used to remove solids to a significant level, a necessary step prior to membrane treatment. A rule of thumb used is to remove suspended solids, and a condition of less than 5 NTU (Nephelometric Turbidity Unit) achieved before using membrane technology cross low filtration to further reduce the accumulation of suspended solids and oil content further down from MF to NF. Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eye, similar to smoke in air. The measurement of turbidity is a key test of water quality. This work tested three types of microfilters namely hollow fiber filters, ceramic and flat sheet microfilters. Figures 4.5 and 4.6 shows the result obtained from these series of tests. The suspended solids removal efficiency ranged from over 88 % to 99 % as membrane pore size decreased from microfiltration to nanofiltration.

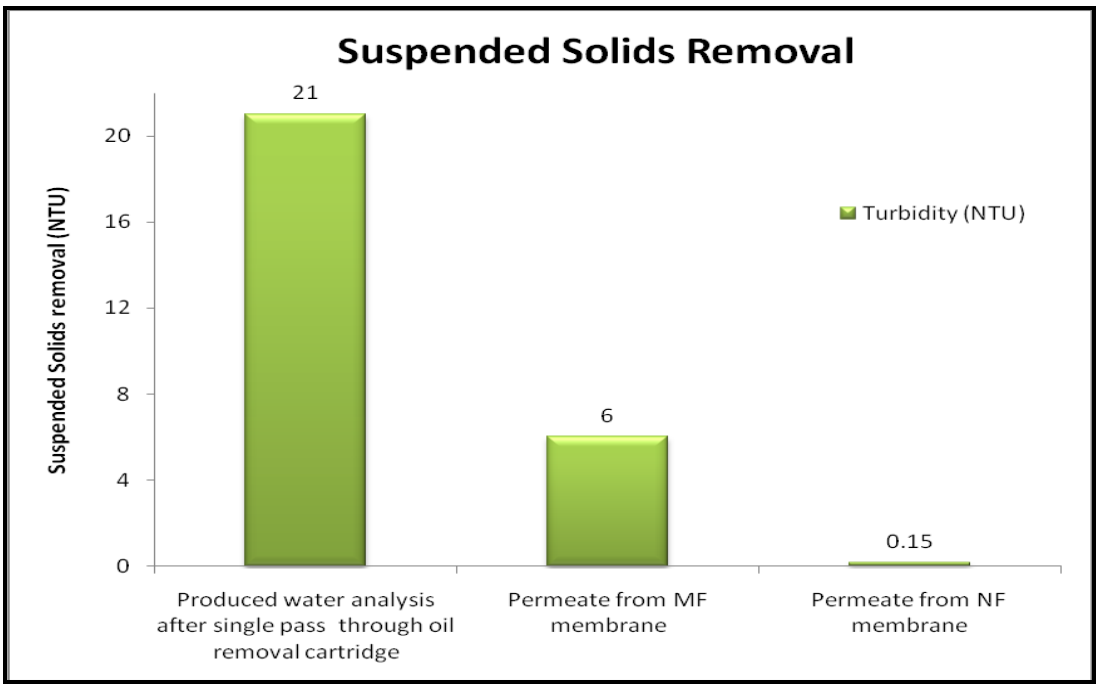


**Fig. 4.5—Solids Removal Efficiency**

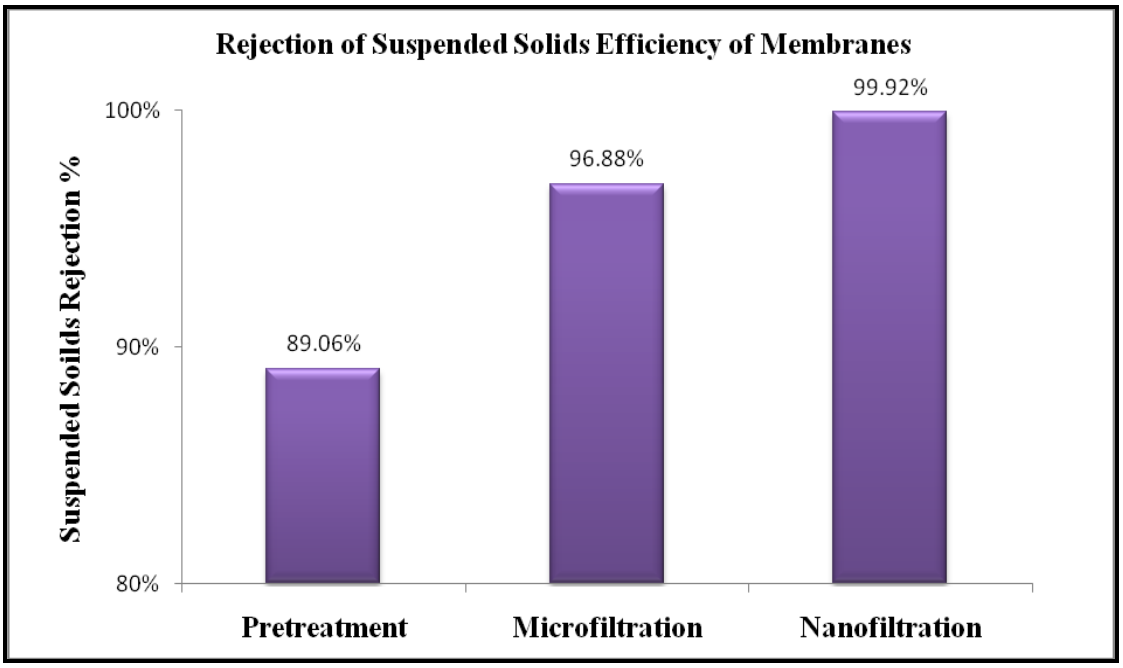


**Fig. 4.6—Percentage Rejection of Suspended Solids**

## 4.3 Softening

Softening involves the reduction of concentration of magnesium, calcium and other ions in water. This treatment lessens or eliminates the ability of water to form scale by solids precipitation when stored in tanks for longer times and also prevents corrosion. Nanofiltration (NF) membranes are permeable to water and monovalent inorganic ions and relatively impermeable to many organics and divalent inorganic ions. A series of tests were performed in this study to test for total dissolved solids removal ability of nanofilters. A sequence of pretreatment with cartridge, oil removal filters and MF membranes was done prior to further treatment using NF. Dow NF flat sheet membranes showed very significant reductions of divalent ions from the tests. Table 1.4 shows a typical result from a series of tests.


**Fig. 4.7—Pictures of Frac Water Before and After Membrane Treatment**

This test was a three step filtration process conducted on oilfield water sample collected from Advanced Hydrocarbon disposal wellsite in college station, Texas. The first step in the treatment was filtration with 10 micron Myclex cartridge filter. It was used to remove large diameter suspended solids and hydrocarbon. The second step was treatment with a 0.2 micron Pall ceramic low pressure filter. This filter showed a reduction in turbidity but did not change the TDS of ion content of the water. It was not expected that the Pall MF membrane would change the TDS of the produced water. The third step was a treatment with a Dow NF 245 membrane and this showed a reduction in TDS and also significant reduction in both anionic and cationic species. Analytical results from this test showed that calcium was reduced from 1636 ppm to 84 ppm, 94.9% removal, magnesium at 98% removal, sodium at 16.5% removal, bicarbonate at 66.4%, sulfate at 91% removal, chloride at 23.1%, and hardness at 95.1%.

From a series of tests, sodium chloride rejections were typically 0% to 20% and divalent inorganic ion rejections varied from 50% to 95% at produced water concentrations. Figure 4.8 is a softening process efficiency graph for Dow NF 245 membrane.

**Table 1.4—Typical Divalent Inorganic Ions in Treated Produced Water**

| Parameter Analyzed | Unit | Pretreatment | Pall MF membrane | Dow NF membrane | % Removal |
|---|---|---|---|---|---|
| Calcium | ($Ca^{++}$) ppm | 1636 | 1670 | 84 | 94.9 |
| Magnesium | ($Mg^{++}$) ppm | 98 | 100 | 2 | 98.0 |
| Sodium | ($Na^{+}$) ppm | 8059 | 8111 | 6731 | 16.5 |
| Bicarbonate | ($HCO_3^{-}$) ppm | 137 | 40 | 46 | 66.4 |
| Sulfate | ($SO_4^{--}$) ppm | 56 | 58 | 5 | 91.1 |
| Chloride | ($Cl^{-}$) ppm | 16608 | 18713 | 12776 | 23.1 |
| Hardness | ($CaC0_3^{++}$) ppm | 4490 | 4580 | 220 | 95.1 |

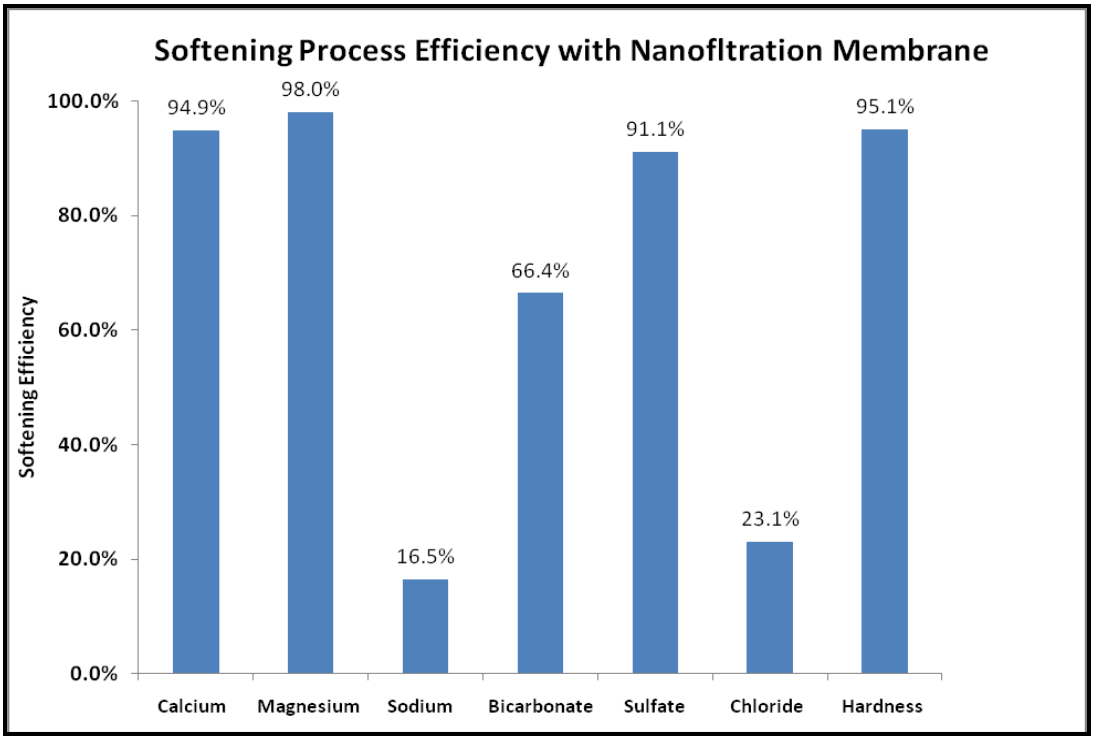


**Fig. 4.8—Softening Efficiency of Produced Water using Nanofiltration Membranes**

## 4.4 Variation in Membrane Flux

This was done to examine how flux and solids removal efficiency were affected by feed water concentration, pressure, time of operation, and temperature. In this work, only minor changes in the solids removal efficiency were observed with slight change in pressure. Each of the membranes was monitored for pressure and flow to allow observation of filter performance. A reduction in permeate flux would indicate fouling of the membrane. In general, analyses showed that while operating pressures were kept constant during the all the tests, removal efficiencies increased with increased temperature and increased flux. Figures 4.9 – 4.11 shows the flux behavior of the hollow fiber, ceramic microfilters, and spiral wound nanofilter for a typical test.

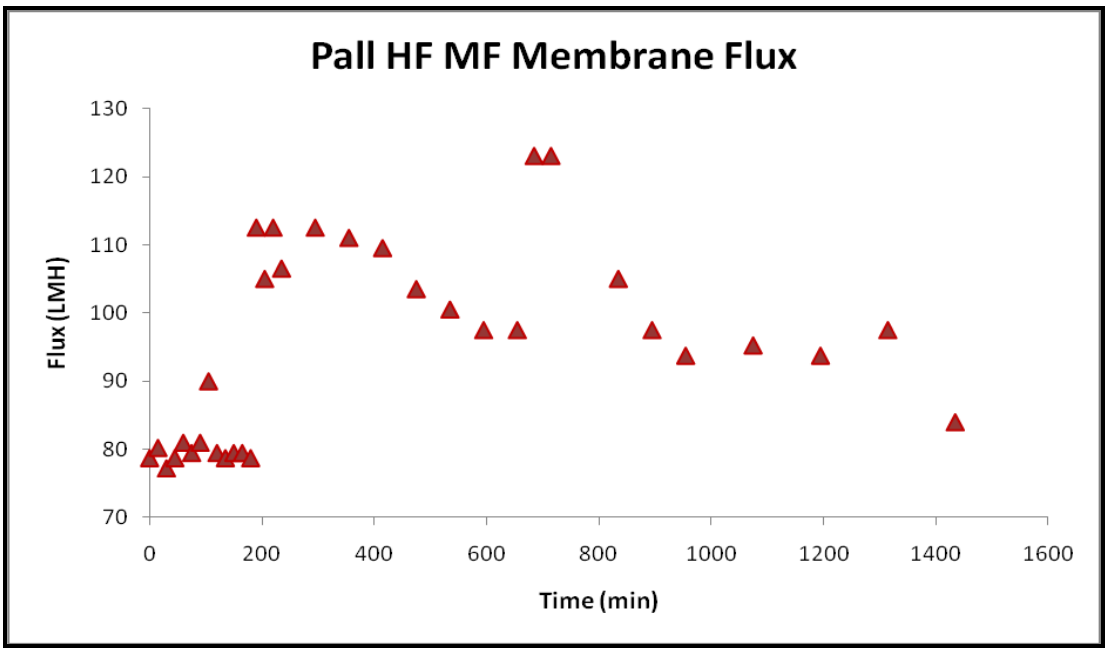


**Fig. 4.9—Flux Performance of a Tested Hollow Fiber Microfilter**

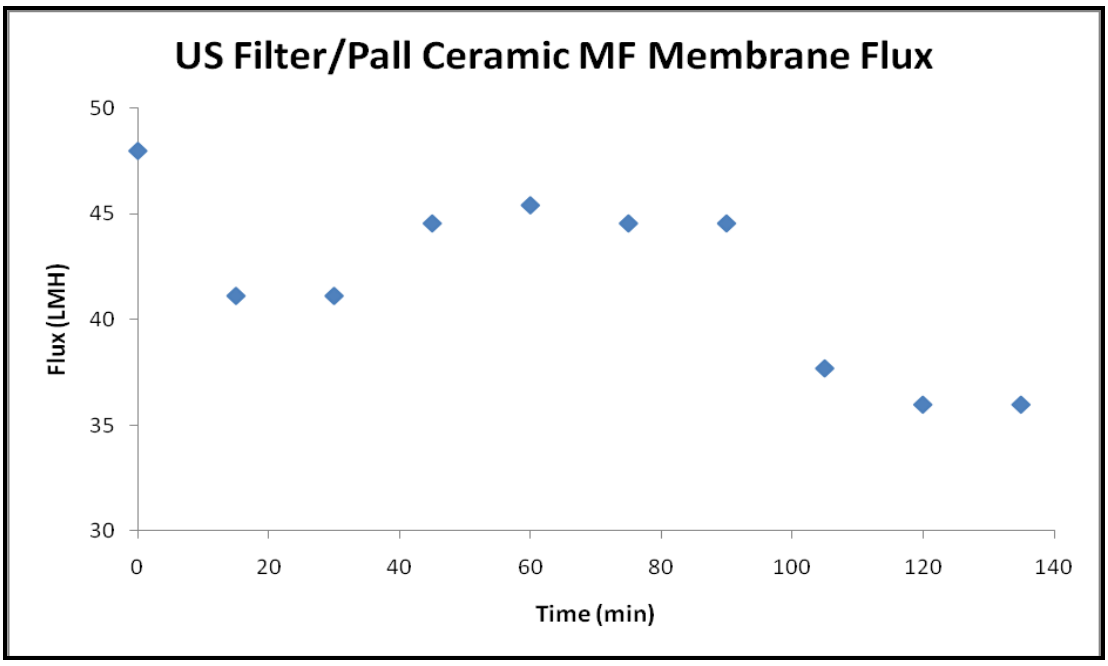


**Fig. 4.10 —Flux Performance of a Tested Ceramic Microfilter**

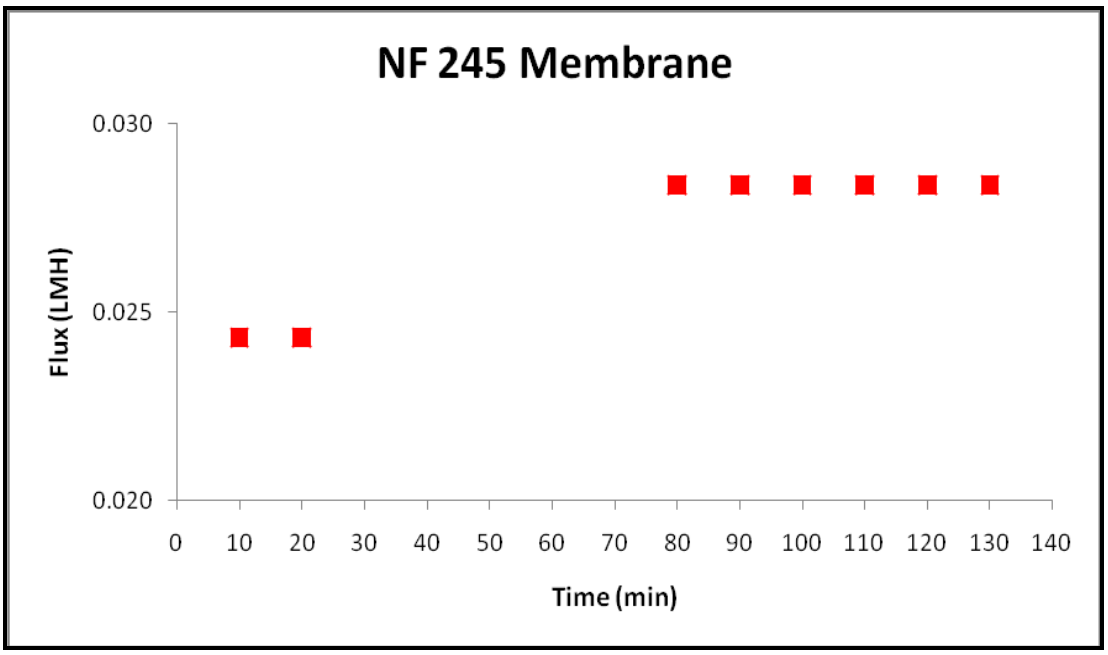


**Fig. 4.11 —Flux Performance of a Tested Nanofilter**

# CHAPTER V

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Membrane treatment of produced water was tested in this work and membranes were selected based on nominal high flux separation efficiency, high tolerance for solids and fluid treatments. Generally, the removal of oil and organic carbon from oilfield produced water depends on the composition of oil-water mixture. Microfiltration membranes showed over 95 % solids rejections measured by turbidity and greater than 80 % oil removal efficiency were obtained in all these tests. Data obtained also proved the use of cartridge filters and microfiltration membranes to be effective as one of the most efficient steps for oil and suspended solids removal in produced water.

Dow NF 245 membranes tested, albeit with lowest permeate flux, produced the highest quality permeate. Nanofiltration membranes proved to be effective in the reduction of total dissolved solids and also significant reduction in both anionic and cationic ions in produced water. Hardness removal was also achieved with nanofiltration membranes. Permeates from the Dow NF 245 membrane treatment showed the best chemical results and acceptable levels of performance of membranes evaluated.

It is important to note that the choice of membrane will depend on the water quality requirement for any particular use considered. From the pilot tests performed in this work, a mobile membrane treatment unit was built for field testing purposes and evaluation of membrane treatment effectiveness.

## 5.2 Recommendations

- It is recommended that membrane treatment of oilfield produced water should be used as a treatment and recycling option to reduce the amount of fresh water requirement for oilfield operations.
- Pretreatment of produced water is required before membrane treatment to reduce fouling tendencies.
- Although fouling and chemical cleaning requirements were not within the scope of this thesis, it is highly recommended that special attention should be paid to fouling and cleaning of membranes in order to improve separation efficiency. Cleaning requirement will be in evidence by a decrease in removal efficiency by the membrane and a permeate flux reduction.
- More attention should be paid to chemical analyses of permeate in order to enable effective evaluation of the efficiency of the entire treatment process.

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# APPENDIX

Series of tests were conducted in a continuous treatment process for various produced water obtained from different frac-water disposal well sources in College Station. Table A1 shows the operating parameters from this test.

**TABLE A1—Example of Membrane Test Flow Parameters (1st & 2nd step treatment)**

| Fluid: Advanced Hydrocarbon Produce Water | | | | Membrane: Pall 0.2 micron ceramic membrane | | Pretreatment: 20 micron Myclex cartridge + 20 micron Hytrex cartridge |
|---|---|---|---|---|---|---|
| **Time** | **Pressure In (psig)** | **Pressure Out (psig)** | **Temp $^{o}$C** | **Permeate Flow (ml/sec)** | **Flow (gpm)** | **Comments** |
| 11:00 | 18 | 2 | 32.5 | 76 | 15 | Water Flux |
| 11:10 | 18 | - | 35.4 | 88 | 15 | Water Flux |
| 11:20 | 17.5 | - | 38.6 | 89.3 | 15 | Water Flux |
| 11:30 | 17.5 | - | 41.5 | 91.3 | 15 | Water Flux |
| 11:40 | 17 | - | 42.8 | 93.3 | 15 | Water Flux |
| Turbidity of Raw Sample = **192 NTU**<br>Turbidity of Pretreated Sample with Hytrex 20 micron cartridge =**100 NTU**<br>Turbidity of Pretreated Sample with Mycelx 20 micron cartridge = **21 NTU** | | | | | | |
| 11:15 | 15.5 | - | 25.9 | 33 | 14 | Clear permeate collected |
| 11:25 | 15 | - | 28.6 | 33 | 14 | Clear permeate collected |
| 11:35 | 15.5 | - | 31.4 | 29.3 | 14 | Clear permeate collected |
| 11.45 | 15 | - | 35.1 | 30 | 14 | Clear permeate collected |
| 11:55 | 15 | - | 37.3 | 29.3 | 14 | Clear permeate collected |
| 12:05 | 15 | - | 40.7 | 24.7 | 14 | Clear permeate collected |
| 12:15 | 15 | - | 45.2 | 23.3 | 14 | Clear permeate collected |
| 12:25 | 15 | - | 48.1 | 22.7 | 14 | Clear permeate collected |

**TABLE A2— Example of Membrane Test Flow Parameters (3rd step treatment)**

| Fluid: Advanced Hydrocarbon Produce Water | | | Membrane: Dow NF 245 membrane | | | PRETREATMENT: Pall 0.2 micron ceramic membrane + 20 micron Myclex cartridge | | |
|---|---|---|---|---|---|---|---|---|
| **Time** | **Pressure In (psig)** | **Pressure Out (psig)** | **Temp °C** | **Total (gal)** | **Recirculation Flow (gpm)** | **Permeate Flow (ml/60sec)** | **Turbidity (NTU)** | **Comments** |
| 14:10 | - | - | - | - | - | - | 8.16 | Feed slightly yellow in appearance |
| 14:20 | 150 | 130 | 28.6 | 11 | 0.621 | 10.5 | 0.15 | clean permeate collected |
| 14:30 | 150 | 130 | 27.8 | 19 | 0.63 | 10 | 0.22 | clean permeate collected |
| 14:40 | 160 | 140 | 27.6 | 23 | 0.63 | 8 | 0.17 | clean permeate collected |
| 14:50 | 160 | 140 | 27.4 | 29 | 0.636 | 11 | 0.20 | clean permeate collected |
| 15:00 | 160 | 140 | 27.5 | 35 | 0.642 | 12 | 0.15 | clean permeate collected |
| 15:10 | 160 | 140 | 27.3 | 41 | 0.638 | 8 | | clean permeate collected |
| 15:20 | 160 | 140 | 27.3 | 48 | 0.637 | 10 | | clean permeate collected |
| 15:30 | 160 | 140 | 27.5 | 55 | 0.636 | 10 | | clean permeate collected |
| 15.40 | 160 | 140 | 27.6 | 60 | 0.639 | 8 | | clean permeate collected |
| 15:50 | 160 | 140 | 27.3 | 64 | 0.632 | 8 | | clean permeate collected |
| 16:00 | 160 | 140 | 27.5 | 69 | 0.637 | 8 | | clean permeate collected |

Table A3 below shows results of a three step filtration process conducted on oil field produced water sample collected at a disposal well site operated by Advanced Hydrocarbon located near College Station, TX. The first step in the treatment was filtration with 10 micron Mycelex cartridge filter. The second step was treatment with a ceramic low pressure microfilter. This filter showed a reduction in Turbidity but did not change the total dissolved solids of content of the water. As expected this filter did not and will not significantly change the organic content of the water as shown by the total inorganic carbon and total organic carbon levels. Treatment was then done with a nanofilter as a third step showing a reduction in total dissolved solids and also significant reduction in both anionic and cationic species contents hereby softening the water.

While the total inorganic carbon value remained the same, the total organic carbon was reduced by about 47 %. The total inorganic carbon in form of hydrocarbons or carbonates was not changed by this filter. Carbonates and Nitrates were at zero level, hence not shown in the table. However a significant reduction in total organic carbon showed that the nanofilter reduced organic content which could be bacteria, proteins, algae or other substances present in the water.

**TABLE A3— Example Treated Water Analysis from Laboratory Test**

| Parameter Analyzed | Units | Myclex Filter Permeate | Microfilter Permeate | Nanofilter Permeate |
|---|---|---|---|---|
| Calcium | (Ca) ppm | 1636 | 1670 | 84 |
| Magnesium | (Mg) ppm | 98 | 100 | 2 |
| Sodium | (Na) ppm | 8059 | 8111 | 6731 |
| Potassium | (K) ppm | 74 | 76 | 61 |
| Boron | (B) ppm | 34.11 | 37.48 | 37.5 |
| Bicarbonate | ($HCO^-_3$) ppm | 137 | 40 | 46 |
| Sulfate | ($SO_4$) ppm | 56 | 58 | 5 |
| Chloride | ($Cl^-$) ppm | 16608 | 18713 | 12776 |
| Phosphorus | (P) ppm ICP | 5.76 | 5.66 | 4.13 |
| pH | | 5.66 | 5.44 | 5.59 |
| Conductivity | umhos/cm | 36600 | 36800 | 25500 |
| Hardness | ppm $CaCO_3$ | 4490 | 4580 | 220 |
| Alkalinity | ppm $CaCO_3$ | 1123 | 33 | 37 |
| Total Dissolved Salts | (TDS) | 26708 | 28810 | 19746 |
| SAR | | 52.3 | 52.1 | 197 |
| Iron (Fe) | (Fe) ppm | 105.13 | 93 | 0.27 |
| Zinc | (Zn) ppm | 0.012 | 0.3 | 0.03 |
| Copper | (Cu) ppm | 0.02 | 0.5 | 0.04 |
| Manganese | (Mn) ppm | 2.37 | 2.4 | 0.15 |
| Turbidity | NTU | 21 | 6 | 0.15 |
| Total Inorganic Carbon | ppm | 25.95 | 26.26 | 25 |
| Total Organic Carbon | ppm | 94.03 | 91.73 | 49.21 |
| Total Carbon Content | ppm | 119.98 | 117.99 | 74.21 |

Table A4 shows an example BTEX removal achieved from treated a water sample from Snook well disposal site in College Station, Texas.

**TABLE A4—Example BTEX Removal Progression Following Volume Treatment with a Microfilter**

| Description | Benzene (ug/l) | Toluene (ug/l) | Ethyl-Benzene (ug/l) | p,m-Xylene (ug/l) | o-Xylene (ug/l) |
|---|---|---|---|---|---|
| Raw Water | 1040 | 1050 | 40 | 287 | 158 |
| 10 gallons flow(MF) | 534 | 410 | 7.4 | 56 | 41 |
| 15 gallons flow(MF) | 518 | 486 | 6 | 50 | 32 |
| 25 gallons flow(MF) | 48 | 3.9 | 0 | 0.3 | 0.5 |

**TABLE A5—Example NPOC Removal Progression Following Volume Treatment with a Microfilter**

| NPOC (Non-Purgeable Organic Carbon) | | |
|---|---|---|
| 10 gallons flow(MF) | 74.8 | ppm |
| 15 gallons flow(MF) | 71.7 | ppm |
| 25 gallons flow(MF) | 79.2 | ppm |
| 25 gallons flow(NF) | 34.8 | ppm |

**TABLE A6—Example Water Chemical Analysis**

| | Unit | Prefiltered feed from Luling TX; 5 micron cartridge | Permeate Luling TX; NF HL Membrane |
|---|---|---|---|
| Calcium ($Ca^{+2}$) | ppm | 1,451 | 298 |
| Magnesium ($Mg^{+2}$) | ppm | 491 | 73 |
| Sulfate ($SO_4^-$) | ppm | 1,461 | 120 |
| Chloride ($Cl^-$) | ppm | 18,381 | 10,820 |
| Conductivity | umhos/cm | 31,600 | 19,050 |
| Hardness | grains $CaCO_3$/gallon | 329 | 61 |
| Hardness | ppm $CaCO_3$ | 5,643 | 1,043 |
| Total Dissolved Salts (TDS) | ppm | 28,047 | 15,984 |
| Copper (Cu) | ppm | 1.12 | 0.47 |
| PH | | 5.94 | 6.37 |

**TABLE A7—Sample Flow Parameters of a Dow NF 245 Membrane**

| Location: TEXAS A & M UNIVERSITY | | | | Membrane: NANO-MEMBRANE (NF 245 FROM DOW CHEMICAL) | |
|---|---|---|---|---|---|
| Fluid: ADVANCED HYDROCARBON PRODUCE WATER | | | | PRETREATMENT: 20micron Cartridge | |
| **Time** | **Pressure In ( psig)** | **Pressure Out (psig)** | **Temp $^{o}C$** | **Permeate Flow (ml/60sec)** | **Comments** |
| 10:10 | 180 | 160 | 20.7 | 7.5ml/60sec | Very clean & clear permeate collected |
| 10:20 | 180 | 160 | 21.2 | 11.5ml/60sec | Very clean & clear permeate collected |
| 10:30 | 180 | 160 | 21.8 | 8ml/60sec | Very clean & clear permeate collected |
| 10:40 | 200 | 180 | 22.3 | 8ml/60sec | Very clean & clear permeate collected |
| 11:00 | 180 | 170 | 23.1 | 7.5ml/60sec | Very clean & clear permeate collected |
| 11:10 | 180 | 170 | 23.7 | 8ml/60sec | Very clean & clear permeate collected |
| 11:20 | 180 | 170 | 24.1 | 8ml/60sec | Very clean & clear permeate collected |
| 11:30 | 180 | 170 | 24.3 | 8ml/60sec | Very clean & clear permeate collected |
| 11:40 | 190 | 180 | 24.8 | 8.5ml/60sec | Very clean & clear permeate collected |
| 11.50 | 190 | 180 | 25.0 | 8ml/60sec | Very clean & clear permeate collected |
| 12:00 | 190 | 180 | 25.4 | 8ml/60sec | Very clean & clear permeate collected |

**TABLE A8—Sample Flow Parameters of a Pall 0.2micron MF Membrane**

| Location: TEXAS A & M UNIVERSITY | | | | Membrane: PALL 0.2 MICRON (MF) | |
|---|---|---|---|---|---|
| Fluid: ADVANCED HYDROCARBON PRODUCE WATER | | | | PRETREATMENT: 20micron Cartridge & 20micron Myclex Cartridge | |
| **Time** | **Pressure In (psig)** | **Temp °C** | **Permeate Flow (ml/min)** | **Flow (gpm)** | **Comments** |
| 13:45 | 6 | 26.8 | 305 | 4 | RO Water Flux (baseline) |
| 13:50 | 6 | 28.8 | 310 | 4 | RO Water Flux (baseline) |
| 14:05 | 5 | 24 | 110 | 4 | Clean and clear permeate was collected |
| 14:25 | 7 | 32 | 110 | 4 | Clean and clear permeate was collected |
| 14:45 | 7 | 38.3 | 110 | 4 | Clean and clear permeate was collected |
| 15:05 | 7 | 43.5 | 110 | 4 | Clean and clear permeate was collected |
| 15:25 | 7 | 47.9 | 110 | 4 | Clean and clear permeate was collected |
| 15:45 | 6.5 | 52.6 | 110 | 4 | Clean and clear permeate was collected |
| 16.05 | 6.5 | 57.4 | 105 | 4 | Clean and clear permeate was collected |
| 16:30 | 6.5 | 60.6 | 105 | 4 | Clean and clear permeate was collected |
| 16:40 | 6 | 30 | 210 | 4 | RO water flux (end of test) |
| 16:45 | 6 | 31.6 | 205 | 4 | RO water flux (end of test) |

# VITA


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